

¹³C NMR Relaxation Study of Internal Rotation of Methyl Groups- Spin-Rotational Relaxation of Methyl Carbon-13 in 2-bromo-p-xylene, 2,5-dimethylanisole and 2,5-dimethylaniline

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In this work we have investigated temperature dependence of spin-rotational relaxation rate, $(1/T_1)_{SR}$, of methyl carbon-13's in 2-bromo-p-xylene, 2,5-dimethylaniline, and 2,5-dimethylanisole and have found that temperature behaviors of two methyl carbon-13's in *ortho*- and *meta*-position, respectively, are substantially different. It has been confirmed that the modified Burke-Chan model proposed by Park et al. can nicely explain different temperature dependence of $(1/T_1)_{SR}$ for these two methyl carbon-13's while the original Burke-Chan model fails to do so.

Introduction

Study of nuclear magnetic relaxation can provide useful informations about molecular motions in liquid^{1,2}. We can also gain valuable insights into rotation of internal rotors such as methyl group by measuring the spin-lattice relaxation time for a nuclear spin located on a such rotor².

Recently, Park et al.³ have measured the spin-lattice relaxation time, T_1 , for methyl carbon-13's in 2-chloro-p-xylene at various temperatures and have found that temperature dependence of T_1 for 1-methyl carbon-13 is substantially different from that for 4-methyl carbon-13. They have also separated the contribution due to spin-rotation mechanism, $(T_1)_{SR}$, from the observed total T_1 via measurement of the NOE factors for each methyl carbon-13 at various temperatures. When they tried to interpret thus obtained $(T_1)_{SR}$ theoretically, they found that temperature dependence of $(T_1)_{SR}$ for 4-methyl carbon-13 could satisfactorily be explained on the basis of Burke-Chan model⁴ while that for 1-methyl carbon-13 could not. In order to explain such different temperature behavior Park et al. have modified the original Burke-Chan model and have applied it to the case of 2-chloro-p-xylene successfully. However, it should be noted that the modified Burke-Chan model proposed by Park et al. has been tested only for the case of 2-chloro-p-xylene and further evidences are necessary in order to have its general applicability established.

In this paper we have investigated temperature dependence of $(T_1)_{SR}$ for methyl carbon-13's in 2-bromo-p-xylene, 2,5-dimethylanisole, and 2,5-dimethylaniline, which are all in liquid state over the temperature range investigated, and have confirmed that the modified Burke-Chan model provide satisfactory explanations of observed temperature dependence of $(T_1)_{SR}$ for methyl carbon-13's in these compounds.

Theory

Spin-lattice relaxation rate, $1/T_1$, for ¹³C in methyl group may be represented as the sum of contributions from ¹³C-H dipolar interaction mechanism, $(1/T_1)_{DD}$, and spin-rotational relaxation mechanism, $(1/T_1)_{SR}$: that is,

$$1/T_1 = (1/T_1)_{DD} + (1/T_1)_{SR} \quad (1)$$

Contributions from other relaxation mechanisms are usually negligible. $(1/T_1)_{DD}$ can be separated out from total relaxation rate, $1/T_1$, through the relation⁵

$$\xi = \frac{\gamma_H}{2\gamma_C} \frac{(1/T_1)_{DD}}{1/T_1} \quad (2)$$

where ξ is the NOE factor for methyl carbon-13, and γ_H and γ_C are, respectively, the magnetogyric ratio for proton and carbon-13.

Substituting Eq.(2) into Eq.(1), we have

$$(1/T_1)_{SR} = (1/T_1) [1 - 2\xi \gamma_C/\gamma_H] \quad (3)$$

Hence, measurements of T_1 and ξ provide the informations of $(1/T_1)_{SR}$.

As has been pointed out by Dubin and Chan⁶, a magnetic nucleus located on an internal top can interact with magnetic fields arising from end-over-end rotation of the entire molecule as well as internal rotation of the top itself. Assuming that modulations of these two types of interactions are mutually independent, Burke and Chan⁴ have derived the following formula for $(1/T_1)_{SR}$ of a nucleus on an internal rotor:

$$(1/T_1)_{SR} = \frac{2kT}{\hbar^2} C^2 I^2 \tau_J + \frac{2kT}{3\hbar^2} (1 - I_a/I_{cc}) I_a C_a^2 \tau_J \quad (4)$$

where

$$I = \text{average of moment of inertia of the molecule} \\ = \frac{1}{3} (I_{aa} + I_{bb} + I_{cc})$$

with I_{aa} , I_{bb} , and I_{cc} being three principal values of inertia tensor of the molecule,

$$I_a = \text{moment of inertia of internal rotor about its axis of rotation,}$$

$$C^2 = \frac{1}{3} (C_{a'a'}^2 + C_{b'b'}^2 + C_{c'c'}^2)$$

with $C_{a'a'}$, $C_{b'b'}$, and $C_{c'c'}$ being three principal values of the spin-overall-rotation coupling tensor, C ,

- C_a = spin-internal rotation coupling constant,
 τ_r = characteristic correlation time for modulation of total rotational angular momentum of the molecule,
 τ_i = characteristic correlation time for modulation of internal rotational angular momentum.

In Eq.(4) it has been assumed that the principal axis of inertia tensor of the molecule that coincides with the axis of internal rotation is the c-axis. The first term on the righthand side of Eq.(4) comes from spin-overall rotation coupling while the second term represents the contribution from spin-internal rotation coupling.

In deriving Eq.(4) Burke and Chan have assumed that end-over-end rotation of the molecule can be described in terms of isotropic rotational diffusion model⁷ and rotational angular momentum correlation time τ_r is shorter than any correlation time for orientational changes involved.

In the rotational diffusion model τ_r may be assumed to be inversely proportional to the viscosity of media, η ; that is,

$$\tau_r \propto \eta^{-1} \quad (5)$$

On the other hand rotation of a highly symmetrical internal rotor such as methyl group is usually assumed to be almost entirely of inertial character⁸. Burke and Chan thus have proposed that τ_r is proportional to $T^{-1/2}$. Therefore, from Eq.(4), we see that temperature dependence of $(1/T_1)_{SR}$ can be explained on the basis of an equation of the following form:

$$(1/T_1)_{SR} = \alpha T \eta^{-1} + \beta T^{1/2} \quad (6)$$

Burke and Chan have assumed that two parameters α and β are virtually independent of temperature and have shown that such assumption is good enough to explain temperature dependence of $(1/T_1)_{SR}$ for ¹⁹F spins in benzotrifluoride. The Burke-Chan model has also been successfully employed by other investigators⁹⁻¹¹ to interpret the spin-rotational relaxation data obtained in their laboratories.

In their recent investigation of spin-lattice relaxation of methyl carbon-13's in 2-chloro-p-xylene, however, Park et al.³ have found that temperature dependence of $(1/T_1)_{SR}$ for 1-methyl carbon-13 cannot be well explained on the basis of Eq.(6) although that for 4-methyl carbon-13 can be treated by the same equation reasonably well. To gain further insight into such different temperature behavior of two methyl groups in the same molecule Park et al. have reexamined the derivation of Eq.(4) and have found that if the correlation time for reorientation of methyl group about its axis of rotation, τ_a , is comparable in magnitude to the rotational angular momentum correlation time, τ_r , Eq.(4) should be rewritten as follows:

$$(1/T_1)_{SR} = \frac{2kT}{3\hbar^2} C^2 I \tau_r \left(1 + \frac{2}{1 + 2\tau_r/\tau_a} \right) + \frac{2kT}{3\hbar^2} (1 - I_a/I_{cc}) I_a C_a^2 \tau_r \quad (7)$$

where the symbols and notations have the same meanings as mentioned previously.

From Eq.(7) we see that Eq.(4), originally derived by Burke and Chan, is valid only in case $\tau_r/\tau_a \ll 1$. The fact that Eq.(6) can explain temperature dependence of $(1/T_1)_{SR}$ for 4-methyl carbon-13 reasonably well but not that for 1-methyl carbon-13 in 2-chloro-p-xylene indicates that for 4-methyl group the

condition $\tau_r/\tau_a \ll 1$ seems to be well valid while for 1-methyl group it does not. The reason for such different behavior of two methyl groups in the same molecule seems to lie in the difference in height of potential barrier to internal rotation.

Although exact theoretical expressions for τ_a and τ_r in the presence of potential barrier to internal rotation are not available, Park et al. have presumed that in the inertial limit both τ_a and τ_r vary with temperature and barrier height approximately as $T^{-1/2} \exp(-V_a/RT)$, where V_a is an activation parameter for internal rotation. They have found that such an assumption is good enough to give adequate explanation of different temperature dependence of $(1/T_1)_{SR}$ for two methyl groups in 2-chloro-p-xylene: Therefore, one may assume that both τ_a and τ_r are slowly varying functions of temperature but their dependency on the potential barrier is rather strong. Since temperature dependency of τ_r is much stronger than that of τ_a , one may regard the latter as independent of temperature in estimating τ_r/τ_a .

Again by assuming that τ_r is inversely proportional to η we have from Eq.(7)

$$(1/T_1)_{SR} = \alpha T \eta^{-1} \left(1 + \frac{2}{1 + \sigma \eta^{-1}} \right) + \beta T^{1/2} \quad (8)$$

where the parameter α is independent of the height of potential barrier while σ and β are not. In other words, α has the same value regardless of the position of methyl group while σ and β take different values for different methyl group. Our interpretation of observed $(1/T_1)_{SR}$ data is based on Eq.(8).

Experimental

The GC grade reagents of 2-bromo-p-xylene, 2,5-dimethylanisole, and 2,5-dimethylaniline were purchased from the Aldrich Chemical Co. and used without further purification. The samples each in a 10mm tube bearing a 5mm inner

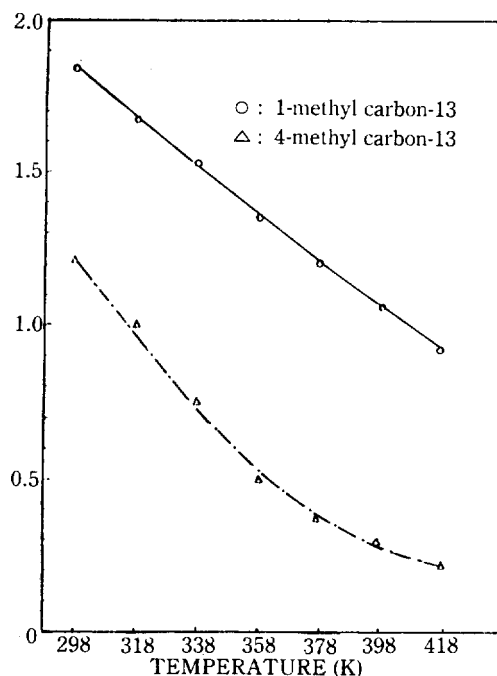


Figure 1. The NOE factor for 1-methyl and 4-methyl carbon-13 in liquid 2-bromo-p-xylene at various temperatures.

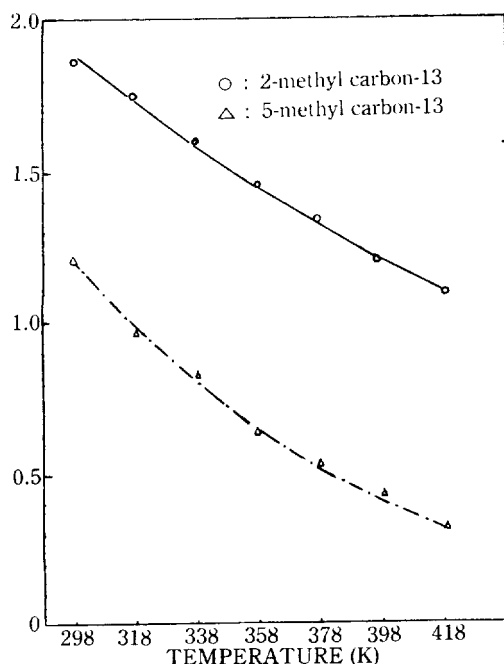


Figure 2. The NOE factor for 2-methyl and 5-methyl carbon-13 in liquid 2,5-dimethylaniline at various temperatures.

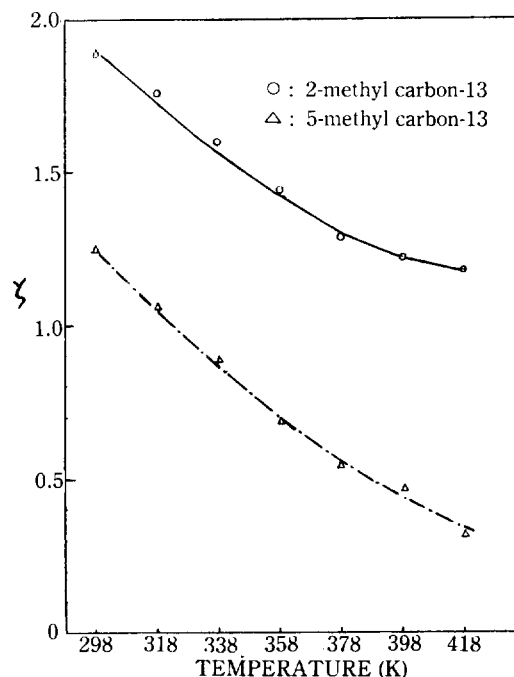


Figure 3. The NOE factor for 2-methyl and 5-methyl carbon-13 in liquid 2,5-dimethylanisole at various temperatures.

coaxial tube filled with a field-lock substance were degassed by repeating the freeze-pump-thaw cycles five times and the tubes were sealed under vacuum. DMSO-d₆ was used as a field-lock substance at high temperature while acetone-d₆ was used at low temperature. Temperature in the probe was measured with the Omega digital thermometer and was maintained within the accuracy of ±1°C throughout the experiment with the aid of variable temperature controller.

All data were obtained with the Bruker WP 80 FT NMR spectrometer operating at 20.12 MHz for ¹³C. The spin-lattice relaxation times for methyl carbon-13's were determined simultaneously by the standard inversion recovery method.^{12,13} The NOE factors were determined by the gated proton noise decoupling technique^{14,15} with a pulse delay of about 10T₁. Both T₁ and ζ were determined from the NMR spectra which were obtained by accumulating 2-5 FID (free induction decay) signals and then performing the Fourier transformation. Each data point shown in Figure 1 through Figure 6 represents an average of at least six independent measurements at the corresponding temperature. In particular, T₁ values were calculated by treating the peak heights with the least square method and only those spectra with reproducibility within ±10% were included in the calculation.

The viscosity data for each sample was measured by making use of the Ostwald viscometer. The procedure for measurement is described in a standard textbook of experimental physical chemistry¹⁶. We have found that the viscosity for 2-bromo-p-xylene, 2,5-dimethylaniline, and 2,5-dimethylanisole can all be expressed in the following form:

$$\eta = \eta_0 \exp(E_a/RT) \quad (9)$$

The observed values of η₀ and E_a are listed in Table 1.

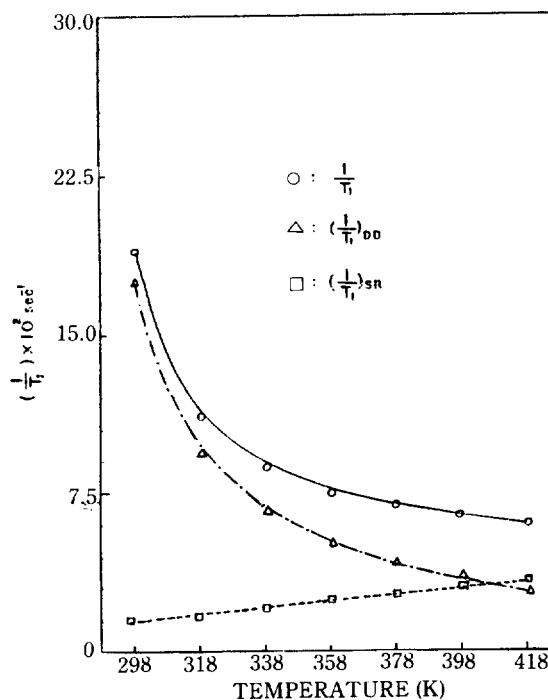


Figure 4. The observed dipolar and spin rotational relaxation rate of 1-methyl carbon-13 in liquid 2-bromo-p-xylene at various temperatures.

Result and Discussions

Experimentally observed values of the NOE factor and the spin-lattice relaxation rate, 1/T₁, are plotted against temperature in Fig. 1. through Fig. 9. Separation of (1/T₁)_{sn} from

Table 1. Viscosity Data

Compounds	η_0 (poise)	E_a (cal/mole)
2-bromo-p-xylene	0.475	1170
2,5-dimethylaniline	0.472	1330
2,5-dimethylanisole	0.454	1180

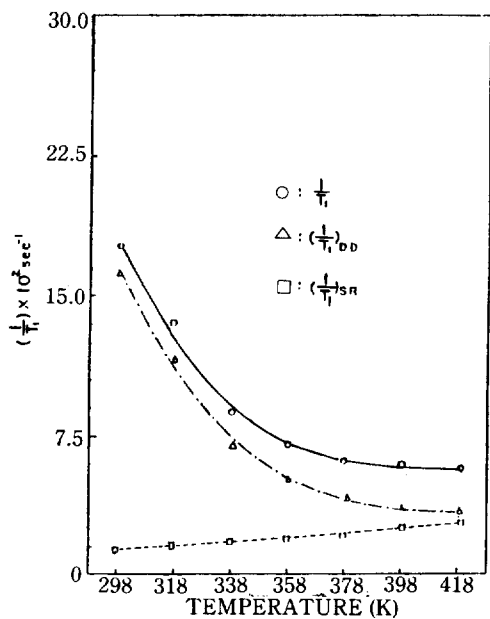


Figure 5. The observed dipolar and spin rotational relaxation rate of 2-methyl carbon-13 in liquid 2,5-dimethylaniline at various temperatures.

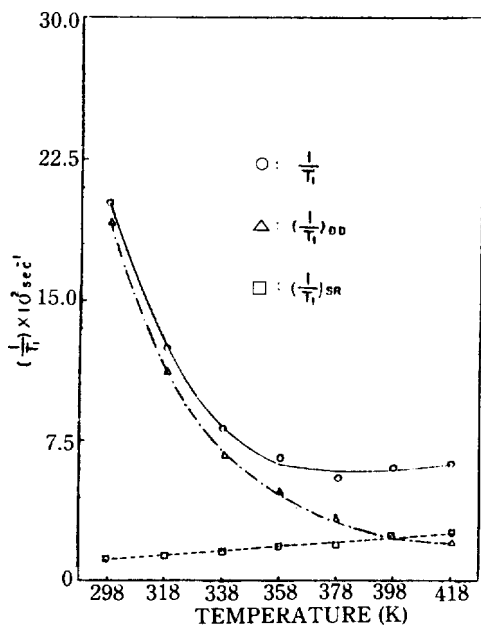


Figure 6. The observed dipolar and spin rotational relaxation rate of 2-methyl carbon-13 in liquid 2,5-dimethylanisole at various temperatures.

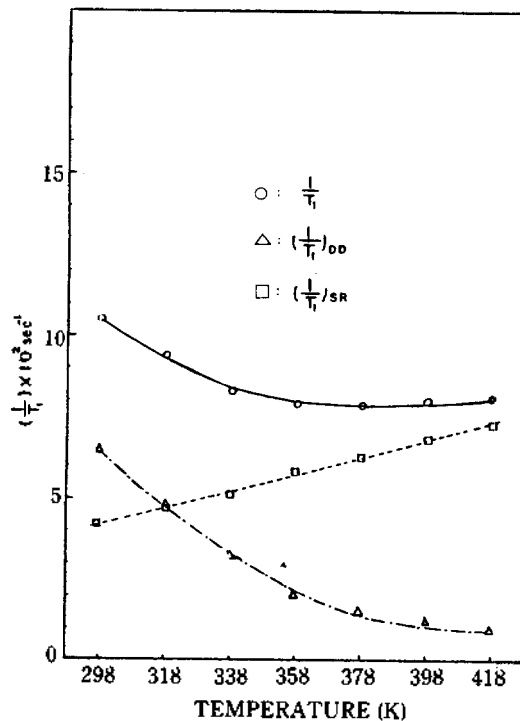


Figure 7. The observed dipolar and spin rotational relaxation rate of 4-methyl carbon-13 in liquid 2-bromo-p-xylene at various temperatures.

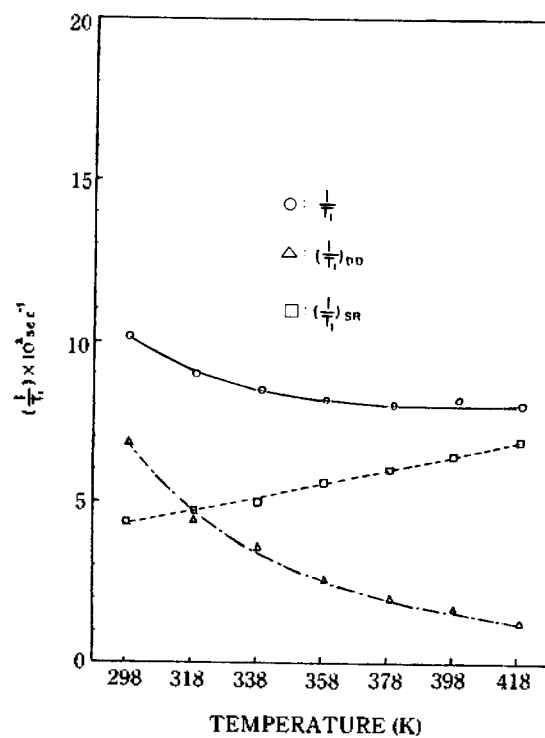


Figure 8. The observed dipolar and spin rotational relaxation rate of 5-methyl carbon-13 in liquid 2,5-dimethylaniline at various temperatures.

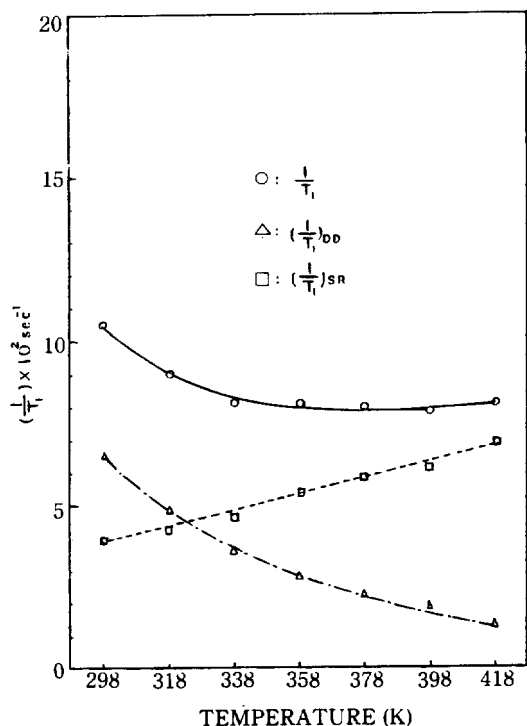


Figure 9. The observed dipolar and spin rotational relaxation rate of 5-methyl carbon-13 in liquid 2,5-dimethylanisole at various temperatures.

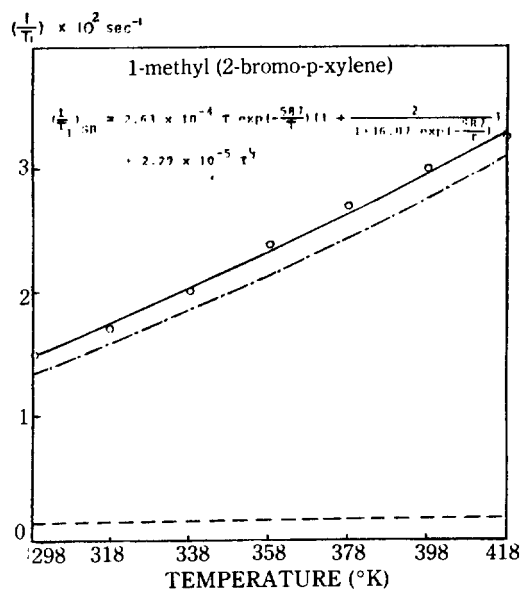


Figure 10. The contributions to $(1/T_1)_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

$(1/T_1)_{DD}$ has been achieved by making use of Eqs.(1) and (3). As previously mentioned, each data point in these figures represents an average of at least six independent measurements at each given temperature. Although the observed data for $(1/T_1)_{DD}$ also deserve due attention, we will leave them for later study and focus our interest only on the interpretation of temperature dependence of $(1/T_1)_{SR}$ in this paper.

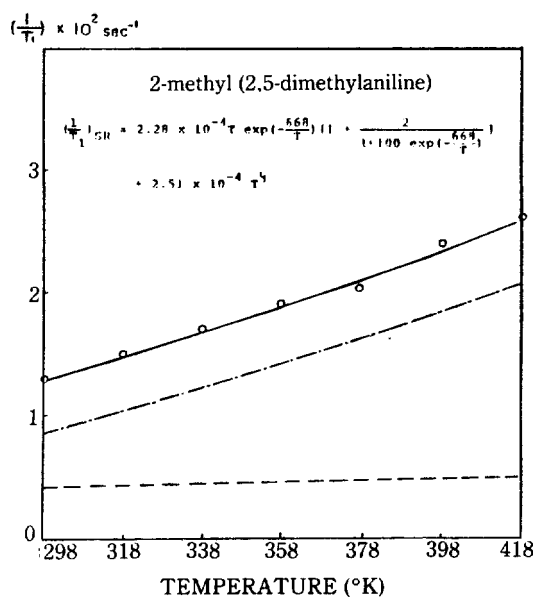


Figure 11. The contributions to $(1/T_1)_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

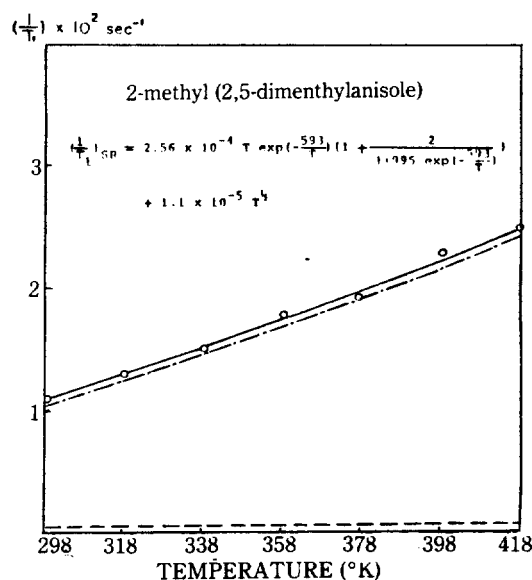


Figure 12. The contributions to $(1/T_1)_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

Observed $(1/T_1)_{SR}$ are fitted to Eq.(8) by the least square method and the results are shown in Fig. 10 through Fig. 15. From these results we see that the parameter α is independent of the position of methyl group in a molecule while σ and β take different values for different methyl group as expected. Two general trends are notable in these figures. First, for the methyl group which is in meta-position to the substituent group the spin-rotational relaxation rate, $(1/T_1)_{SR}$, is larger than for the methyl group in ortho-position and the contribution from the spin-internal rotation coupling to $(1/T_1)_{SR}$ is also substantially larger than for the latter case. This indicates that

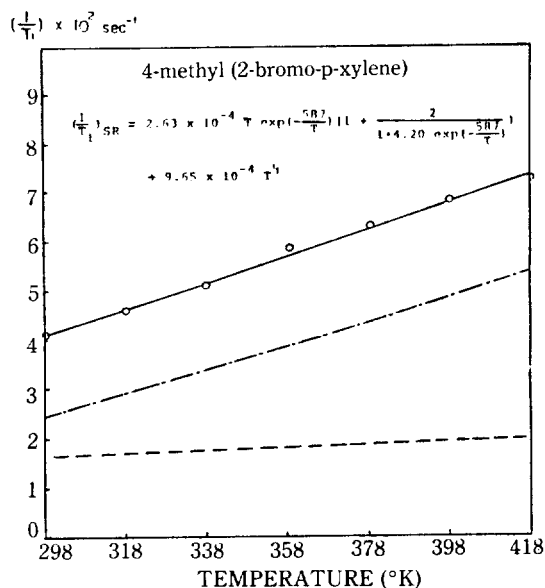


Figure 13. The contributions to $(\frac{1}{T_1})_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

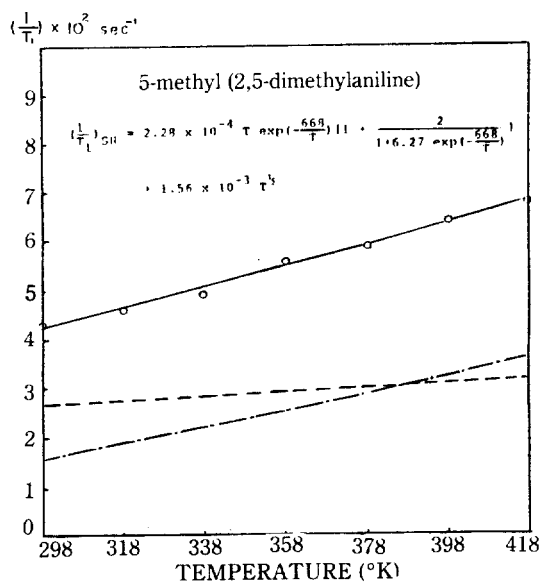


Figure 14. The contributions to $(\frac{1}{T_1})_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

the methyl group ortho to the substituent group suffers more hindrance to its internal rotation in accordance with expectation from steric consideration. Second, in all of the three compounds investigated it has been found that the spin-internal rotation contribution to total $(1/T_1)_{SR}$ increases much more slowly than the contribution due to spin-overall rotation coupling. This means that for these compounds rotation of methyl groups can be treated in the inertial limit while end-over-end rotation of the entire molecule may better be described in the rotational diffusion limit.

One might be tempted to acquire informations regarding

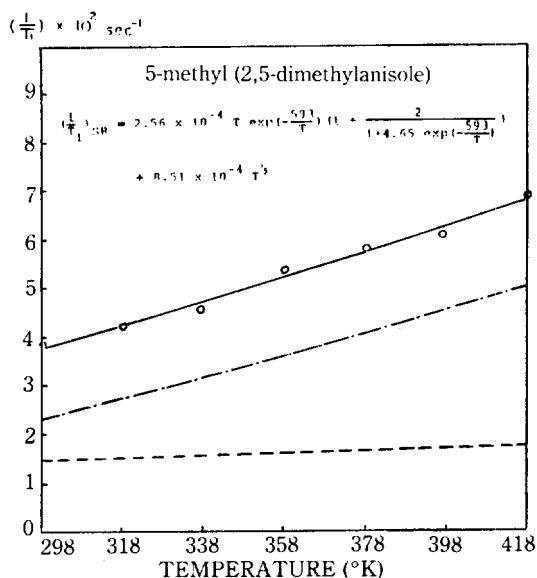


Figure 15. The contributions to $(\frac{1}{T_1})_{SR}$ from spin internal rotation coupling (---) and spin overall rotation interaction (—) are separately depicted.

the height of potential barrier by comparing the parameters β and σ for two methyl groups. Unfortunately, however, our presumption that both τ_i and τ_o vary as $T^{-1/2} \exp(-V_i/RT)$ is only of qualitative nature at best and cannot be directly used to obtain such quantitative informations. It is our hope, however, that intensive study of these parameters may reveal a way to extract some useful quantitative informations regarding the potential barrier to internal rotation.

In conclusion it has been confirmed that the modified Burke-Chan model proposed by Park et al. can nicely explain temperature dependence of $(1/T_1)_{SR}$ for methyl groups in 2-bromo-p-xylene, 2,5-dimethylaniline, and 2,5-dimethylanisole which cannot be well described on the basis of original Burke-Chan model.

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References

1. F. Noack, in "NMR, Basic Principles and Progress" (P. Diehl, E. Fluck, and R. Kosfeld, Eds) Vol. 3, Springer-Verlag, Berlin (1971).
2. D. A. Wright et al., in "Topics in Carbon-13 NMR Spectroscopy" edited by G. C. Levy, Vol. 3, Wiley-Interscience, New York (1979).
3. K. S. Park, Master of Science Thesis, Seoul National University (1985), unpublished. J. W. Lee and K. S. Park, to be published.
4. T. E. Burke and S. I. Chan, *J. Magn. Reson.* **2**, 120 (1970).
5. K. F. Kuhlmann and D. M. Grant, *J. Am. Chem. Soc.* **90**, 7355 (1968).
6. A. S. Dubin and S. I. Chan, *J. Chem. Phys.* **46**, 4534 (1967).
7. R. E. D. McClung, *J. Chem. Phys.* **51**, 3842 (1969).
8. R. E. D. McClung, *J. Chem. Phys.* **57**, 5478 (1972).
9. C. F. Schmidt, Jr., and S. I. Chan, *J. Magn. Reson.* **5**, 151 (1971).

10. R.F. Parker and J. Jonas, *J. Magn. Reson.* **6**, 106 (1972).
11. W. Suchanski and P. S. Canepa, *J. Magn. Reson.* **33**, 389 (1979).
12. H. Gunther, *NMR Spectroscopy*, Wiley & Sons, 1980. See Chap. VII.
13. R. K. Harris, *Nuclear Magnetic Resonance*, Pitman Books Ltd. See Chap. 3.
14. R. Freeman and H. D. W. Hill, *J. Chem. Phys.* **51**, 3140 (1969).
15. R. K. Harris and R. H. Newman, *J. Magn. Reson.* **24**, 449 (1976).
16. D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry", McGraw-Hill Kogakusha, Tokyo, 1967; F. Daniels *et al.*, "Experimental Physical Chemistry", McGraw-Hill Kogakusha, Tokyo, 1970.

Kinetic Studies on the Reduction of 1-Benzyl-3-cyanoquinolinium Cations by Sodium Borohydride and the Applicability of Marcus Theory

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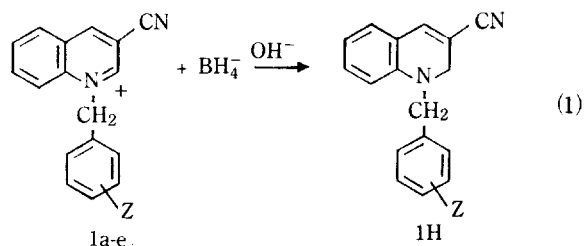
The reduction of a series of 1-substituted benzyl-3-cyanoquinolinium ions (*p*-CH₃, H, *p*-Br, *m*-F, *p*-CN) by sodium borohydride has been investigated. In all cases the products from these reactions were found to be 1,2-dihydroquinolines over 82% yields. Rates of reduction were measured in basic condition and in solvent system consisting of 4 parts of isopropyl alcohol and 1 part of water by volume. Second order rate constants were obtained for these reactions. When the ratio of [OH⁻] to [BH₄⁻] becomes large the observed rate constants (*k*_{obs}) decrease by a small factor. Reaction scheme and rate law are discussed.

Brønsted α ($= \frac{d \ln k}{d \ln K}$) obtained by using the value of equilibrium constant *K*, which was obtained previously, was not 0. Instead, a value of 0.36 was obtained which indicated that the reduction by borohydride was structure-dependent according to the Marcus formalism even though the reaction rate was close to the diffusion limit.

Introduction

Sodium borohydride (NaBH₄) has been commonly employed as a mild reducing agent for organic synthesis¹⁻³. Yet the kinetic study of the reaction of NaBH₄ (BH₄⁻) is rarely investigated. It seems that NaBH₄ is not a suitable substrate for kinetics because of its much hygroscopic property which makes it very difficult to weigh quantitatively. In addition, reactions with BH₄⁻ usually take place too fast to be monitored by conventional methods. In present paper we report the reduction of 1-substituted benzyl-3-cyanoquinolinium ion (Q⁺, **1**) by BH₄⁻ as shown in eq. (1), which was conducted in NaOH solution.

It is generally considered that the hydride transfer step is the rate determining for the hydride transfer reaction.



a, *p*-CH₃. b, H. c, *p*-Br. d, *m*-F. e, *p*-CN.

However, the rate determining step in the present system is in question according to the result of *k*_{obs} vs. [OH⁻]/[BH₄⁻] and it will be discussed in detail. Marcus theory⁵⁻⁷ is applied to the present system in which two reactants have opposite charges.

Experimental

Compounds **1a-e** are known substances which were prepared by addition reaction of 3-cyanoquinoline with corresponding benzyl bromides at about 120°C and identified by their physical and spectroscopic properties⁸. In neutral or acidic solution both reactions of BH₄⁻ with H⁺ and with **1** are extremely rapid so it would be very difficult to measure the rate of the reaction of **1** with BH₄⁻. For this reason 4.4 M-NaBH₄ dissolved in 14 N-NaOH solution (purchased from Alfa Chemical Co.) was used for the kinetic measurements and they were all made in basic solutions because such solutions are stable⁹. Thus, the BH₄⁻ concentration was directly proportional to the OH⁻ concentration in most of the reaction mixtures. However, some experiments were performed with added NaOH to deconvolute the effect due to the ratio of these two concentrations.

The major reaction product (82%) was 1,2-dihydroquinoline (**1H**) which has an absorption at 415 nm, the longest wavelength observed among dihydroquinolines. The remain-