Measurement of Methyl Barriers to Rotation from ^{13}C Spin-Rotation Relaxation Times

A. P. Zens and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received December 4, 1974*

Abstract: The ^{13}C spin-rotation relaxation times for several methyl compounds were determined. A relationship between $T_{1,SR}$ and reported spectroscopic barriers to rotation was found to exist. A semiempirical relationship, $T_{1,SR} = 25.61(1 + 0.382V_0)$, between $T_{1,SR}$ and barriers to rotation at 38° was developed. The average deviation of the calculated to reported barrier was ±0.1 kcal/mol. The advantages of this method are in its general applicability to organic molecules and its time advantages over other spectroscopic methods.

Spin-lattice relaxation times offer a method of studying the microdynamics of molecules. Unfortunately the precise details of a molecule's dynamic behavior are not readily available[1] because of a general inability to partition the observed T_1 ($T_{1,obsd}$) into contributions from specific motions of a molecule. It is thus evident that the measurement of methyl barriers to rotation from spin-lattice relaxation times might prove to be a difficult if not a futile task. Attempts to measure the hindered rotation of methyl groups using spin-lattice relaxation times has emphasized this fact.[2,3] Lyerla and Grant,[2] using ^{13}C NMR and Woessner's[4] anisotropy equations for molecules which undergo small step diffusion as an ellipsoid with internal motion, had to assume isotropic diffusion for the molecules under study in order to complete the necessary barrier calculations. The results of their study showed a correlation between T_1 dipole-dipole relaxation times and barriers to rotation for methyl groups, but even with this overall correlation there was a noticeable exception to their results.[5] Solid phase proton relaxation studies also suffer from similar problems in determining barrier heights. Here in addition to the uncertainty of the contributions from intermolecular forces to the barrier height, concern must be focused on the contribution of intermolecular terms to $T_{1,obsd}$ and also the dominance of the methyl groups C_3 motion vs. other motions which might not be frozen out at low temperatures. Kumar and Johnson[3] have recently shown that activation energies calculated from proton relaxation studies in the solid phase are in general lower than gas phase barrier determinations by spectroscopic method.

In terms of the above mentioned facts ^{13}C spin-rotation spin-lattice relaxation appears to circumvent the above dilemma since the $T_{1,SR}$ relaxation mechanism is dominated by the motion of the methyl top about its C_3 axis.[6-8] This dominance of ^{13}C $T_{1,SR}$ by the C_3 motion of the methyl group and the cited increase in $T_{1,SR}$ values with the decreasing rotational angular momentum of methyl tops by several authors[9-11] supports the feasibility of measuring methyl barriers to rotation from $T_{1,SR}$ relaxation times. The results of an initial study are reported herein.

Experimental Section

Materials and Sample Preparation. The 2-butyne, isopropyl chloride, acetonitrile, ethyl iodide, and 1,1,1-trichloroethane were obtained from Columbia Organics. The dimethyldichlorosilane and 1-penten-3-yne were purchased from PCR, Inc., and Chemical Samples, Co., respectively. The toluene and methyl formate were purchased from Matheson Coleman and Bell, and the acetic acid was obtained from J. T. Baker. The internal lock material used in these experiments was either cyclohexane-d_{12} (Aldrich) or acetone-d_6 (Merck Sharp and Dohme). The compounds studied in our laboratory were distilled or fractionated on a low-temperature vacuum column[12] prior to use. The samples were prepared neat in 8-mm NMR tubes except for a small amount of lock material ≈5%. The height of the liquid in the NMR tubes was 4 cm. In addition to these samples of known barrier to rotation a 2.0-g sample of camphor (Fisher Scientific) was prepared in 1.8 ml of acetone-d_6. All of the NMR samples were degassed by five freeze-thaw cycles at 10^{-5} Torr on a vacuum line.

NMR Measurements. The ^{13}C T_1's were determined on a Varian CFT-20 NMR spectrometer equipped with 16K of core and a Sykes 120 Compu/Corder. The ^{13}C resonance frequency was 20 MHz. The T_1's were measured using the 180°-τ-90° pulse sequence.[13] Each T_1 was determined with the average of four S_∞ determinations and each τ value represents the accumulation of at least 20 180°-τ-90° pulse sequences with a 5 T_1 total delay between sequences. The Nuclear Overhauser Effect enhancement factors η_{CH}, NOE − 1, of the methyl carbons were determined using the NOE suppress gated decoupling technique.[14] The acquisition time used for the NOE studies was less than 5 sec in all cases. This was done to avoid radiofrequency heating of the sample from high-power decoupling of protons when the decoupler is gated on. During these experiments the decoupler was on less than 5% of the total time (acquisition time and pulse delay). As a further check against the possibility of radiofrequency heating influencing the observed NOE the η_{CH} of acetonitrile was measured with the decoupler turned off and was found to be within experimental error of the value obtained using the NOE suppress technique. The temperature for the T_1 and NOE experiments was determined by use of a calibrated thermocouple both before and after an experiment. The temperature in all cases was 38 ± 0.5°. The area of each methyl resonance for the NOE and T_1 experiments was determined by use of a Geotec compensating polar plainimeter. The T_1 data were treated by a standard linear least-squares analysis. In addition to the experiments performed on the Varian CFT-20 spectrometer a separate determination of the $T_{1,obsd}$ and η_{CH} for 2-butyne was made on a Varian XL-100-15 operating at 25 MHz. The dedicated data system employed with this spectrometer is a 16K (1K = 1024 words) 620I computer with a two million word disk (VDM-36). The purpose of this experiment was to access any possible difference between single (CFT-20) and crossed (XL-100) coil instruments on η_{CH} and $T_{1,obsd}$. It was also desirable to measure the contribution of gas-liquid interchange on $T_{1,obsd}$ and η_{CH} for these experiments.[15,16] The $T_{1,obsd}$ for 2-butyne would probably be most susceptible to this form of interaction since its boiling point is 11° below the actual temperature of the T_1 experiment. To quench the effects of gas-liquid phase interactions a microcell[17] was employed in measuring the T_1 and NOE of 2-butyne on the XL-100. The 2-butyne and lock solvent were thoroughly degassed on a vacuum line and condensed into the microcell and sealed. The results in Table I show that there is a negligible difference between the $T_{1,obsd}$ and NOE determined on either instrument.

Results and Discussion

Table I shows the observed T_1, the NOE enhancement factors, η_{CH}, the contribution of spin-rotation, $T_{1,SR}$, to $T_{1,obsd}$, the reported barrier to rotation V_0, and the calcu-

Table I. Experimental $T_{1,\mathrm{obsd}}$, $T_{1,\mathrm{SR}}$, $\eta_{\mathrm{C-H}}$, the Reported Spectroscopic Barrier to Rotation (V_0), and the Calculated Barrier to Rotation (V_0) for the Methyl Compounds under Investigation[l]

Compd	$T_{1,\mathrm{obsd}}$	η_{CH}	$T_{1,\mathrm{SR}}$	V_0 (lit.)	V_0 (calcd)
$CH_3C_6H_5$	17.4	0.63	25.5	0.014[a]	−0.01
CH_3CN	20.4	0.46[k]	26.5	0.0[b]	0.09
$(CH_3)_2C_2$[m]	17.2	0.58	24.3	0.0[c]	
$(CH_3)_2C_2$	16.9	0.59	24.0	0.0[c]	−0.16
$CH_3C_2C_2H_3$	16.9	0.71	26.0	0.0[d]	0.04
CH_3COOH	10.2	1.35	31.8	0.43[e]	0.63
CH_3OOCH	23.2	0.70	35.8	1.19[f]	1.04
$(CH_3)_2SiCl_2$	13.5	1.42	49.7	2.56[g]	2.46
CH_3CH_2I	16.1	1.47	61.7	3.68[h]	3.69
$(CH_3)_2CHCl$	21.6	1.37	69.4	4.33[i]	4.48
CH_3CCl_3	12.5	1.67	78.0	5.40[j]	5.36
Camphor					
C-8	8.9	1.67	55.5		3.05
C-9	9.5	1.66	57.5		3.26
C-10	9.2	1.66	55.7		3.08

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lated barrier to rotation at 38°. The $T_{1,\mathrm{SR}}$ values in Table I measured in our laboratory were calculated directly from the $T_{1,\mathrm{obsd}}$ and η_{CH} values by assuming that the dipole-dipole and spin-rotation terms are the only mechanism available for relaxation of a methyl carbon

$$T_{1,\mathrm{obsd}}^{-1} = T_{1,\mathrm{DD}}^{-1} + T_{1,\mathrm{SR}}^{-1} \tag{1}$$

This assumption is reasonable since it has been shown that methyl carbon T_1's do not exhibit a field dependence.[2] The $T_{1,\mathrm{SR}}$ values were thus obtained by the standard formula

$$T_{1,\mathrm{SR}}^{-1} = T_{1,\mathrm{obsd}}^{-1} - T_{1,\mathrm{obsd}}^{-1}\,[2\gamma_{\mathrm{C}}\eta_{\mathrm{CH}}/\gamma_{\mathrm{H}}] \tag{2}$$

Here γ_{C} and γ_{H} are the magnetogyric ratio for ^{13}C and ^1H, respectively.

The $T_{1,\mathrm{SR}}$ values in Table I show a clear trend of increasing values as the barrier to internal rotation increases. It is also evident that all the methyl tops investigated which are essentially free rotors have the same $T_{1,\mathrm{SR}}$ values within experimental error.

To see how $T_{1,\mathrm{SR}}$ values for methyl tops are related to the internal rotational barrier, we shall use the formalism adopted by Wang and coworkers[8,18] for a symmetric top under conditions of extreme narrowing

$$T_{1,\mathrm{SR}}^{-1} = \frac{8\pi^2 kT}{3\hbar^2}\left[(C_\parallel I_\parallel)^2\frac{\tau_\parallel}{I_\parallel} + 2(C_\perp I_\perp)^2\frac{\tau_\perp}{I_\perp}\right] \tag{3}$$

Here $C_\parallel$ and $C_\perp$ are the spin-rotation interaction coupling constants (in Hz)[19] parallel and perpendicular to the C_3 rotational axes, $\tau_\parallel$ and $\tau_\perp$ are the spin-rotation interaction correlation times for motion of the molecule about its parallel and perpendicular axes, $I_\parallel$ and $I_\perp$ are the moments of inertia about the parallel and perpendicular axes, $\hbar$ is Planck's constant divided by 2π, and kT is the Boltzmann factor. Equation 3 may be further simplified by noting that

$$\tau_\parallel/I_\parallel \gg \tau_\perp/I_\perp$$

and that these ratios differ by an order of magnitude.[8] Therefore, eq 3 can be reduced to eq 4,

$$T_{1,\mathrm{SR}}^{-1} = \frac{8\pi^2 kT}{3\hbar^2}\{C_\parallel{}^2 I_\parallel \tau_\parallel\} \tag{4}$$

which shows to a good approximation that $T_{1,\mathrm{SR}}$ for a methyl top is governed by the motion of the top about its C_3 axis. From eq 4 it is thus evident that any alteration of the motion of a methyl top about its C_3 axis, e.g., a change in the barrier to rotation in going from one compound to another, should be reflected by a change in their respective $T_{1,\mathrm{SR}}$ values. This observation is subject to the constraint that $C_\parallel$ and $I_\parallel$ are relatively constant from compound to compound.[20] A relationship between spin-rotation coupling constants and ^{13}C chemical shifts has been demonstrated by several authors.[21-23] It is our belief that $C_\parallel$ is essentially constant for all methyl tops since the σ_{zz} component (parallel to the C_3 axis) of the shift tensor for methyl compounds is nearly constant. This is confirmed by the calculated σ_{zz} values for CH_3OH, CH_3F, CH_3NH_2, and C_2H_6 which vary by less than 2%.[24] These results have been shown to be in accord with the experimental data of Pines, Gibby, and Waugh.[25,26]

In order to formulate a clearer picture of how a barrier to internal rotation can effect the $T_{1,\mathrm{SR}}$ value of a methyl top, it is necessary to consider how an increase in the hindrance to rotation of a methyl top would effect the coupling between the methyl carbon nuclear spin and the internal rotational magnetic field generated by the C_3 motion of the top.[9,18,27] Equation 5 relates $T_{1,\mathrm{SR}}^{-1}$ to the angular momentum (subject to the conditions implied by eq 4) of the relaxing nucleus.

$$T_{1,\mathrm{SR}}^{-1} = \frac{8\pi^2 C_\parallel}{3\hbar^2}\int_0^\infty \cos(\omega_0\tau)\, e^{-2D_\perp\tau}\langle J\cdot J(t)\rangle\, d\tau \tag{5}$$

Here $J(t)$ is the rotational-angular momentum of the molecular unit in which the spin resides evaluated at time t, ω_0 is the Larmor frequency, $D_\perp$ is the molecular diffusion tensor perpendicular to the top axis, τ is the correlation time for molecular reorientation, the brackets represent the ensemble average over the thermal distribution of the methyl top at an arbitrary initial time, and $C_\parallel$ is the spin-rotation coupling tensor for internal rotation.[18,28]

From eq 5 it can now be seen how $T_{1,\mathrm{SR}}$ is influenced by the internal barrier to rotation for a methyl top. One would expect the ensemble average to be quenched in the limit of high barriers, as confirmed by the increase of $T_{1,\mathrm{SR}}$ values in Table I. Of perhaps more interest is the fact that for methyl tops which are not subject to a barrier to internal rotation the ensemble average should be at a constant and maximum value along with the subsequent value of $T_{1,\mathrm{SR}}^{-1}$. Thus one would expect that the methyl $T_{1,\mathrm{SR}}$ values of 1-penten-3-yne, methyl cyanide, 2-butyne, and toluene should be the same, barring any possible effects of viscosity from sample to sample on the ensemble average. The experimental values of $T_{1,\mathrm{SR}}$ for these zero barrier compounds appear to verify this hypothesis.

In order to show a more quantitative relationship between V_0, the barrier height, and $T_{1,\mathrm{SR}}$ it is necessary to evaluate the ensemble average $\langle J \cdot J(t) \rangle$. This quantity has been represented by Hubbard and Wang as[18,28]

$$\langle J \cdot J(t) \rangle = (kT/I_{\parallel})I_{\parallel}^{2}e^{-t/\tau_{SR}} \tag{6}$$

where, τ_{SR} is the angular momentum correlation time about the C_3 axis, kT is the thermal energy of the top about this axis, and $I_{\parallel}$ is the moment of inertia of the top about its C_3 axis. In eq 6 it can be seen that representing the thermal energy as kT has neglected the possibility of a potential term V which represents the degree of quenching of the angular momentum by a barrier to rotation.[29] If we now substitute $kT + V$ for kT in eq 6 and substitute these results for $\langle J \cdot J(t) \rangle$ in eq 5 and evaluate in the limit of the extreme narrowing condition we obtain eq 7. The correlation time is

$$T_{1,ST}^{-1} = \frac{8\pi^2(kT + V)}{3\hbar^2} I_{\parallel}C_{\parallel}^{2}\tau_{SR} \tag{7}$$

now equated to the period of free rotation through one radian as given by the equipartition theory

$$\tau_{SR} = n(I_{\parallel}/kT)^{1/2} \tag{8}$$

Here n is used as a empirical parameter which relates this gas phase quantity to that of solution.[6,8] It is seen that eq. 8 also lacks a potential term. The inclusion of a potential term and subsequent substitution into eq 7 results in the following expression for $T_{1,SR}^{-1}$.

$$T_{1,SR}^{-1} = \frac{8\pi^2(kT + V)^{1/2}I_{\parallel}^{3/2}C_{\parallel}^{2}n}{3\hbar^2} \tag{9}$$

The dependence of $T_{1,SR}$ in eq 9 as a function of the barrier height for a methyl rotor cannot be explicitly calculated due to a lack of suitable knowledge about the dependence of V on the barrier height. For this reason the potential V is equated to the semiempirical function $f(V_0)$ where V_0 is the barrier height such that

$$(kT + V)^{1/2} = (kT)^{1/2}f(V_0) \tag{10}$$

Substituting these results into eq 9 and taking the reciprocal gives a relationship that expresses $T_{1,SR}$ as a function of V_0 (eq 11).

$$T_{1,SR} = \frac{3\hbar^2 f(V_0)}{8\pi^2 I_{\parallel}^{3/2}C_{\parallel}^{2}(kT)^{1/2}n} \tag{11}$$

In order to gain insight on how $T_{1,SR}$ varies as a function of barrier height a plot of $T_{1,SR}$ vs. barrier height was made. Figure 1 reveals that $T_{1,SR}$ varies *nearly linearly* with increasing barrier height. The function $f(V_0)$ in eq 11 is of now replaced, as Figure 1 suggests, by a linear function of V_0 (eq 12).

$$1 + \alpha V_0 \tag{12}$$

Here α is a constant which is determined by the slope of the least-squares fit. Substitution of eq 12 with $\alpha = 0.382$ and the value of 25.61 for the constants into eq 11 will now yield a semiempirical expression for the dependence of $T_{1,SR}$ on V_0 at 38°. Using eq 13, the barrier to rotation is now determined directly from the $T_{1,SR}$ value of the methyl tops under investigation.

$$T_{1,SR} = 25.61(1 + 0.382)V_0) \tag{13a}$$

$$V_0 = (T_{1,SR} - 25.61)/9.783 \tag{13b}$$

It is important to note that the numerical constants employed in eq 13 are highly dependent upon the temperature at which the experiment was performed. Table I compares the reported barrier to rotation reported by spectroscopic methods with those calculated by use of eq 13b. As a practical example of the utility of this method the methyl carbons of camphor (I) were investigated. Table I reveals that the measured barrier to rotation for the three methyl carbons is nearly the same (≈3.1 kcal/mol). The exact nature of the source of hindrance for these methyl rotors is beyond the scope of this paper. However, it is important to note that this method has made analysis of methyl rotor hindrance accessible to larger and more complex molecules than by other spectroscopic methods.

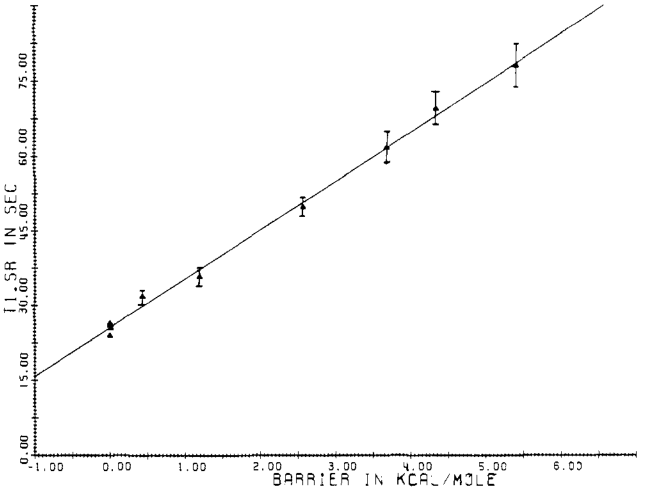
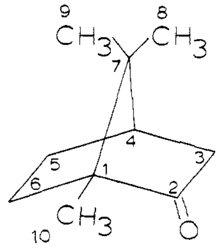


Figure 1. A linear least-squares fit of $T_{1,SR}$ vs. reported spectroscopic barrier to rotation plot. The error bars for the zero barrier compounds where omitted for clarity. The horizontal and vertical bars denote an estimated limit of experimental error in the measurement of $T_{1,SR}$.



Limitations and Advantages. It should be emphasized that the empirical relationship established in eq 13 is only valid at 38°. Other limitations of this method appear to be its applicability to compounds which contain methyl groups with spin systems other than protons, i.e., ^{19}F and ^{31}P, since the time saving technique of separating $T_{1,SR}^{-1}$ from $T_{1,obsd}^{-1}$ can no longer be facilitated by use of NOE parameters.[31] Further precautions must be taken when applying this method to methyl carbons that can undergo chemical exchange since in such cases the measured value of $T_{1,SR}$ reflects the average of two different chemical species.[21,23] It should also be mentioned that in cases where the moment of inertia of the methyl top about its C_3 axis is not significantly less than the moment of inertia about some other axis of the molecule, the spin rotation relaxation times may no longer be dominated by the C_3 motion of the methyl top.

The advantage of this method is in its applicability to methyl containing molecules which do not lend themselves to normal spectroscopic barrier determination. It is the authors' contention that this technique should show considerable promise in application to molecules which contain methyl tops that are believed to be subject to steric hindrance. A comparison of the methyl $T_{1,SR}$ of toluene to that of a severely hindered methyl rotor should yield ratios >3. One further advantage of this method is that using the experimental conditions cited in this paper, several T_1 determinations and NOE enhancement factors can be determined in a 24-hr period, thus representing a considerable time advantage over spectroscopic methods for determining the rotational barrier of a methyl top.

Finally, it should be noted that some degree of caution should be exercised when comparing gas phase spectroscopic barrier values with those determined in the liquid and solid phases. We have recently measured the methyl barriers for isobutene, *trans*-2-butene, and *cis*-2-butene and found some variance between published gas phase values[36] and the values we determined in the liquid phase. However, in all cases the values fell between the published gas and solid phase values.[33-35]

Summary and Conclusions

From the above discussion it is concluded that $T_{1,\mathrm{SR}}$ values for methyl tops are strongly influenced by their internal barrier to rotation. The use of eq 13 for determining barriers to rotation for the compounds under investigation yielded an average deviation from the reported spectroscopic values of ±0.10 kcal/mol. This result has prompted further and continuing investigation into the feasibility and application of this method to methyl tops. It is also noted that similar applications should be feasible with other threefold rotors, e.g., CF_3, SiH_3, and SiF_3 groups.

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Exciplex and Triplex Emission in the System 9,10-Dichloroanthracene–2,5-Dimethyl-2,4-hexadiene[1a,b]

Jack Saltiel,*[1c] David E. Townsend,[1c] Brant D. Watson,[1d] and Patrick Shannon[1c,d]

Contribution from the Department of Chemistry, and the Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306. Received December 6, 1974

Abstract: Steady-state and transient fluorescence measurements have been made using mixtures of 9,10-dichloroanthracene and 2,5-dimethyl-2,4-hexadiene in benzene and acetonitrile. In benzene a fluorescent exciplex, $\lambda_{\max}$ ~485 nm, τ 7.4 nsec, forms reversibly with an estimated equilibrium constant for exciplex formation at room temperature of 20 ± 1 M^{-1}. In contrast, no exciplex fluorescence is observed from acetonitrile solutions at intermediate diene concentrations, but triplex fluorescence $\lambda_{\max}$ ~543 nm and τ 3.6 nsec, is observed at higher diene concentrations. Steady-state fluorescence observations in the presence of air are also described.

The green luminescence observed upon excitation of 9,10-dichloroanthracene (DCA) in benzene solutions containing 2,5-dimethyl-2,4-hexadiene (DMH) has been attributed to fluorescence from a DCA-DMH exciplex.[1b] Exciplexes are thought to arise generally from the interaction of aromatic hydrocarbons and dienes,[2] and have been postulated to collapse to adducts[3-5] and to provide additional pathways for reaction of one of the partners with other molecules.[1b] Since such exciplexes are rarely fluorescent[6] a more detailed study of the DCA-DMH system was under-