lifetime of pyrene in HDTCl micelles is considerably shorter than for nitrogen-purged or vacuum-degassed cyclohexane solutions. Furthermore, the fluorescence lifetime of pyrene in HDTBr micelles is shorter than in HDTCl micelles and the longest fluorescence lifetimes are found for pyrene solubilized in STS micelles. Thus, our results with pyrene are qualitatively similar to those for naphthalene, except that the solubility of pyrene in water was so small in our experiments that no ultraviolet absorption from aqueous pyrene could be detected.

We also point out that excimer emission can complicate fluorescence analysis in the case of pyrene. In the concentration range used for our experiments (10^{-6} to 10^{-7} *M*) no excimer emission was observed. Further work is in progress to elucidate the role of oxygen quenching in micellar environments.

Conclusions

In summary, although our work is somewhat preliminary in nature, we believe that our results demonstrate that use of time-correlated studies will be capable of affording considerable understanding of phenomena occurring in micelle solutions including both dynamic and structural information by *direct* observation of processes in the micelle phase and bulk solution. The use of micelle-forming detergents to organize and direct chemical reactions is generally based on measurement of some average property of the solution. In most, if not all, previous studies, it has been necessary to assume that a dissolved substrate is totally associated with the micelle or to deduce from kinetic analysis the magnitude of the observed properties which derive from the micellar and aqueous phases. Some interesting effects, which have been previously unrecognized, are suggested by this work. There appears to be a difference in the effective oxygen concentrations in the hydrocarbon core of different micelles. This could result from either a lower (kinetic or equilibrium) concentration of oxygen in the micellar interior or from a tremendous decrease in the quenching constants for aromatic singlet states by oxygen in a micellar environment. The "catalysis" and "inhibition" of quenching of singlet states by oxygen have been put forth and are supported by the strong quenching of solubilized naphthalene fluorescence by bromide ion in cationic micelles and the resistance to bromide ion quenching of naphthalene solubilized in anionic micelles. It is also possible that water is playing a special role in quenching naphthalene fluorescence; *i.e.*, water penetration is greater into the cationic micelle than into the anionic micelle.[27]

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Nuclear Spin Relaxation in Di-*tert*-butyl Nitroxide

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Abstract: Measurements of the transverse and longitudinal relaxation times of the protons in the di-*tert*-butyl nitroxide radical have been made at a series of radical concentrations and at three different frequencies. The relaxation times are accounted for by intermolecular and intramolecular electron–proton interactions. The intermolecular contribution to the relaxation times is explained in terms of the electron–proton dipole–dipole interaction. The intramolecular dipolar interaction is used to account for the longitudinal relaxation times, while the transverse relaxation times are determined by both the dipolar interaction and the Fermi contact interaction.

The interaction of the unpaired electrons on transition-metal ions or organic free radical with nuclear spins provides an efficient mechanism for nuclear spin relaxation. Investigations of nuclear relaxation times can provide information on electron–nuclei separations, scalar coupling between the spins, and correlation times for molecular motion. There have been a number of studies of the intermolecular interaction between the electron spins on transition-metal ions and solvent nuclei.[2] Intermolecular electron–nuclear interactions between organic free radicals and solvent nuclei have also been investigated.[3] A study of the relaxation times of the protons in di-*tert*-butyl nitroxide has been reported.[4] The nuclear relaxation times are normally dominated by the electron–nuclear dipole–dipole and Fermi contact interactions. The dipolar interaction can be modulated by rotational or translational motion or by various types of exchange interactions. The Fermi contact interaction is modulated by interactions which affect the lifetimes of the electron spin states.

Nuclear magnetic resonance spectra of organic radicals can be obtained from molecules in which the lifetimes of the electron spin states are short compared with the reciprocal of the hyperfine splitting constant.[5] In this case, the hyperfine field generated by the electron at the nucleus is rapidly averaged and one observes a

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single line (from each set of equivalent nuclei) which is shifted from the position of a corresponding diamagnetic peak by

$$\Delta H = -A(\gamma_e/\gamma_n)\left(\frac{g\beta H}{4kT}\right) \qquad (1)$$

where A is the hyperfine splitting constant. The electron spin energy levels can be average by the intermolecular spin exchange reactions. In this case, the lifetime of the electron spin states is given by

$$t_e = 1/k[c] \qquad (2)$$

where k is the rate constant for spin exchange and [c] is the radical concentration. Rate constants for spin exchange between the neutral radicals have been found to be of the order of $10^9\ M^{-1}\ \mathrm{sec}^{-1}$.[6]

In concentrated radical solutions both intermolecular and intramolecular electron–nuclear interactions can contribute to nuclear relaxation times. The intermolecular contribution is proportional to the fraction of radical in the solution and should increase with increasing radical concentration. The intramolecular contribution decreases with increased radical concentration because of the inverse concentration dependence of t_e. The dipolar and Fermi interactions may contribute to both the intermolecular and intramolecular terms.

The work reported in this paper concerns a determination and analysis of the relaxation times of the protons in the di-*tert*-butyl nitroxide (DBNO) radical. The transverse (T_2) and longitudinal (T_1) relaxation times of the protons in this radial were determined at a series of concentrations. Experiments were carried out at three frequencies to determine the frequency dependence of the relaxation times. The hyperfine coupling constant for the protons can be determined from the nmr spectrum ($A = 0.1$). Electron spin resonance has previously been used to obtain the rate constant for spin exchange[6] ($k = 3.7 \times 10^9$) and to estimate the rotational correlation time[7] ($t_r \sim 10^{-11}$ sec). Bond angles and bond lengths in this radical have been determined from an electron diffraction study.[8]

The equations which we have used to account for the transverse and longitudinal relaxation times of the protons in DBNO were first developed by Solomon and Bloembergen.[9] These equations can be used to describe the contribution of both intermolecular and intramolecular electron–nuclei dipolar and scalar interactions to the relaxation times. The Solomon–Bloembergen equations can be written as

$$\left(\frac{1}{T_1}\right) = PC_1\left(\frac{1}{r^6}\right)\left[3t_c + \frac{7t_c}{1 + \omega_s^{\,2}t_c^{\,2}}\right] + PC_2A^2\left[\frac{t_e}{1 + \omega_s^{\,2}t_e^{\,2}}\right]$$

$$\left(\frac{1}{T_2}\right) = {}^1\!/_2PC_1\left(\frac{1}{r^6}\right)\left[7t_c + \frac{13t_c}{1 + \omega_s^{\,2}t_c^{\,2}}\right] + {}^1\!/_2PC_2A^2 \times \left[t_e + \frac{t_e}{1 + \omega_s^{\,2}t_e^{\,2}}\right]$$

$$C_1 = \frac{4}{30}S(S+1)\left[\frac{g^2\beta^2g_N^{\,2}\beta_N^{\,2}}{\hbar^2}\right] \qquad C_2 = \frac{2}{3}\frac{S(S+1)}{\hbar^2}$$

$$\frac{1}{t_c} = \frac{1}{t_r} + \frac{1}{t_e}$$

In these expressions P is 1 for the intramolecular interactions and the ratio of radical to solvent concentrations for the intermolecular interactions. The average electron–nuclear separation is given by r, A is the electron–nuclear hyperfine splitting constant, ω_s is the electron's Larmor frequency, t_r is the rotational correlation time, and t_e is the correlation time for spin exchange.

The concentration-dependent terms in these equations are t_e, which varies with the reciprocal of concentration, and P, which varies linearly with concentration (for the intermolecular interaction). The concentration in our experiments was varied from 5.95 to 0.19 M. If one takes k equal to 3.7×10^9 then t_e varies from 4.5×10^{-11} to 1.4×10^{-10} sec.

The scalar term in the expression for $1/T_1$ is proportional to $(1 + \omega_s^{\,2}t_e^{\,2})^{-1}$. At 100 MHz this term has a minimum value of 353 while at 25 MHz the minimum value is 23. The scalar interaction makes a negligible contribution to T_1 because of the large magnitude of this term. The scalar term in the expression for $1/T_2$ contains $t_e + [t_e/(1 + \omega_s^{\,2}t_e^{\,2})]$. A large contribution from the scalar interaction is predicted at large values of t_e because of the first term in this expression.

The dipolar expressions for both $1/T_1$ and $1/T_2$ contain terms proportional to $(1 + \omega_s^{\,2}t_c^{\,2})^{-1}$. In the extreme in which $\omega_s^{\,2}t_c^{\,2} \ll 1$ one predicts equal dipolar contributions to $1/T_1$ and $1/T_2$. When $\omega_s^{\,2}t_c^{\,2} \gg 1$ the ratio of the dipolar contributions to T_1 and T_2 is 7/6. In the intermediate case in which $\omega_s^{\,2}t_c^{\,2}$ is of the order of unity, one predicts a frequency dependence for both T_1 and T_2.

The variables in the expressions for $1/T_1$ and $1/T_2$ include t_r, t_e, A, and r. The hyperfine splitting constant for DBNO can be obtained from its nmr spectrum while t_e can be determined from the rate constant for spin exchange. Estimates of rotational correlation times have been obtained from esr investigations. We have used the value of A and t_e and varied t_r and r to obtain at best fit to our experimental data.

Experimental Section

The di-*tert*-butyl nitroxide was synthesized by the technique of Hoffmann.[10] The radical was estimated to be between 95 and 98% pure from constant wave nmr spectra. The small amount of diamagnetic impurity produced a small error in our measurements of T_2 at 25 MHz. All of the experiments were carried out with CCl_4 as the solvent at 25°.

Spin-lattice relaxation times were measured at 25.1 and 100 MHz with a 180°–τ–90° pulse sequence. T_2's were measured at 25.1 MHz by the Carr–Purcell[11] method as modified by Meiboom and Gill.[12] The data from the pulse experiments were treated with an

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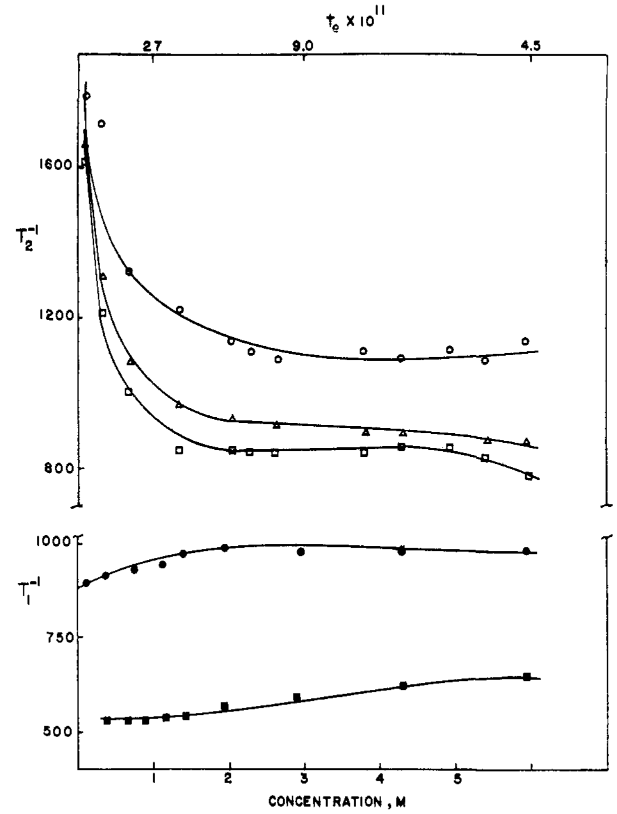

Figure 1. Experimental values of $1/T_1$ and $1/T_2$ *vs.* concentration at the various frequencies: (○) is $1/T_2$ at 25 MHz, (△) is $1/T_2$ at 60 MHz, (□) is $1/T_2$ at 100 MHz, (●) is $1/T_1$ at 25 MHz, (■) is $1/T_1$ at 100 MHz.

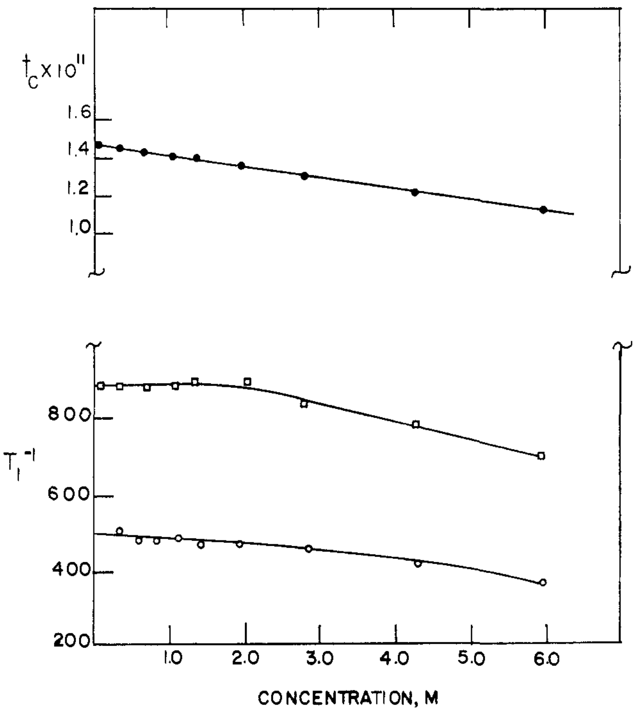

Figure 2. Intramolecular spin–lattice relaxation times *vs.* concentration: (○) is $1/T_1$ at 100 MHz, (□) is $1/T_1$ at 25 MHz. The upper part of the plot shows t_c *vs.* concentration (●).

exponential least squares computer program to obtain values for T_1 and T_2. Transverse relaxation times were measured at 100 and 60 MHz from the line widths of spectra taken on high resolution nmr spectrometers.

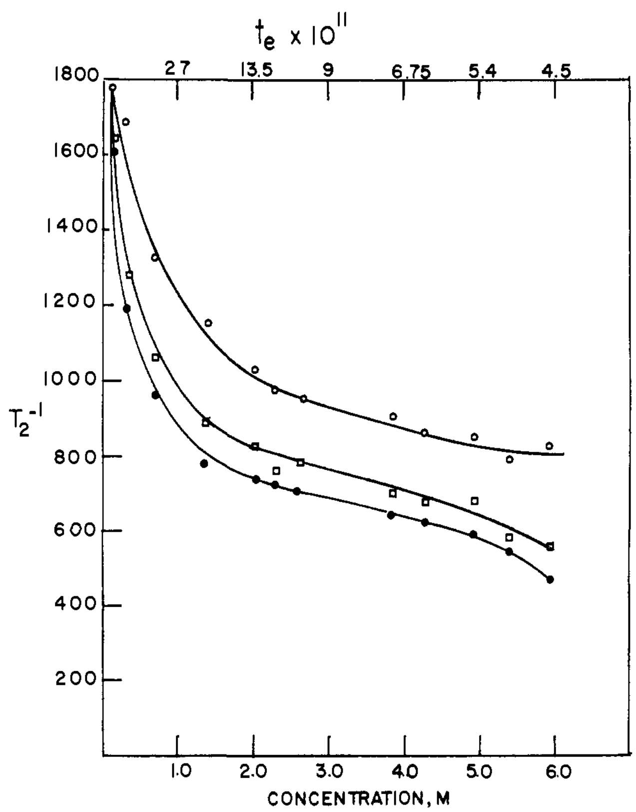

Figure 3. Intramolecular transverse relaxation times *vs.* concentration: (●) is $1/T_2$ at 100 MHz, (□) is $1/T_2$ at 60 MHz, (○) is $1/T_2$ at 25 MHz.

The line width and susceptibility shifts of peaks from the protons in benzene and tetramethylsilane (TMS) were measured at 60 and 100 MHz at a series of DBNO concentrations. The shifts were measured with respect to an external reference and indicated that there was no contact interaction between these protons and the electron on DBNO. The intermolecular dipolar contribution to the transverse relaxation times of the protons in these molecules was 53.4 $\sec^{-1}$ (mol DBNO)$^{-1}$ at both frequencies.

Results and Discussion

The experimental values of $1/T_1$ and $1/T_2$ at the various frequencies and at a series of radical concentrations are shown in Figure 1. The x axis of this plot shows both the concentration and the value of t_e. The experimental data reflect the contributions of both the intermolecular and intramolecular terms to T_1 and to T_2. The sharp increase in $1/T_2$ at lower radical concentrations is due to a large contribution from the Fermi contact term which becomes important when t_e is sufficiently long. The spin–lattice relaxation time varies slowly with concentration over the range investigated, indicating that the scalar term does not make a significant contribution to T_1. Both T_1 and T_2 are found to depend on the magnetic field strength. The field dependence reflects the relative magnitude of $1 + \omega_s^2 t_c^2$ in the dipolar term.

In order to separate the intermolecular and intramolecular contributions to T_1 and T_2, we have assumed that the intermolecular contribution can be approximated by the dipolar relaxation of solvent protons (benzene or TMS) by DBNO. The intermolecular term is relatively large at high concentrations and this approximation may be incorrect if either the electron–proton separation or the rotational correlation time for

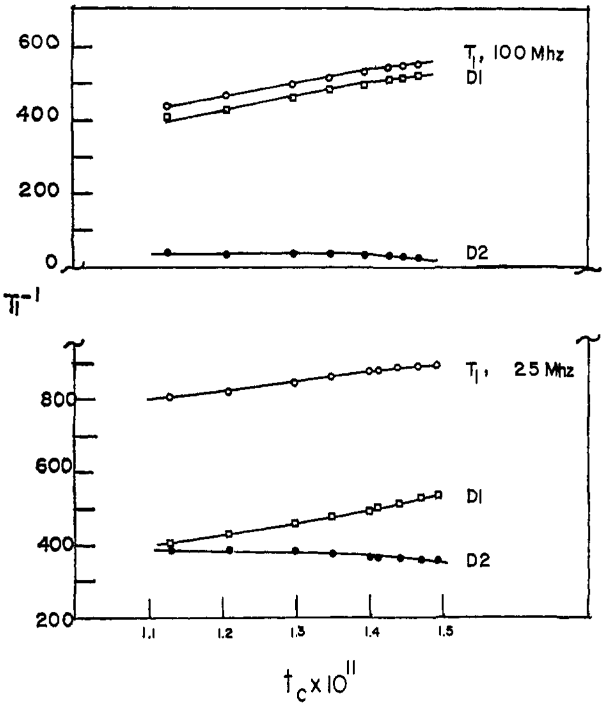

Figure 4. Plots of D_1, D_2, and intramolecular spin–lattice relaxation times *vs.* t_c; (○) is $1/T_1$, (□) is D_1, (●) is D_2.

a DBNO–solvent pair is different from that of a DBNO–DBNO pair. Gutowsky's work[3] on the relaxation of solvent protons by DBNO has shown that the ratio of T_1/T_2 is nearly 7/6 at 28 MHz. This work indicates that the $\omega_s^2t_c^2$ for the intermolecular interaction should be large compared with unity at higher frequencies. We have calculated intermolecular spin–lattice relaxation times from our values for intermolecular T_2's and this ratio.

Values of intramolecular T_1's and T_2's were obtained by subtracting the intermolecular contribution from the experimental points. Plots of intramolecular T_1's and T_2's are shown in Figures 2 and 3. Figure 2 also shows the variation of t_c with concentration. These plots were fit with theoretical curves to determine values for t_r and r. The value obtained for t_r by this technique is 1.5×10^{-11} sec while r is found to be 3.57 Å.

The intramolecular spin–lattice relaxation times can be explained solely in terms of the electron–proton dipolar interaction. The value of T_1 varies slowly with concentration and then approaches a constant value at lower concentrations. This behavior reflects the variation of t_c with t_e. At higher concentrations t_e is small enough to contribute to the value of t_c, but as the concentration is lowered t_e becomes large compared with t_r and t_c approaches the value of t_r.

The variation of T_1 with concentration and with frequency is complicated by the presence of t_c in both the numerator and denominator of the dipolar term in eq 3. To obtain the relative magnitudes of the two parts of the dipolar expression we define

$$D_1 = C3t_c/r^6$$

$$D_2 = (C7t_c/r^6)(1 + \omega_s^2t_c^2)$$

Plots of D_1 and D_2 *vs.* t_c (concentration) are shown in Figure 4. At 100 MHz, D_2 is small because of the large value of $\omega_s^2t_c^2$ (22 to 38) and T_1 is determined mainly by D_1. At 25.1 MHz, $\omega_s^2t_c^2$ varied from 2.3 to 3.3 over the concentration range investigated and D_1 and D_2 make comparable contributions to T_1.

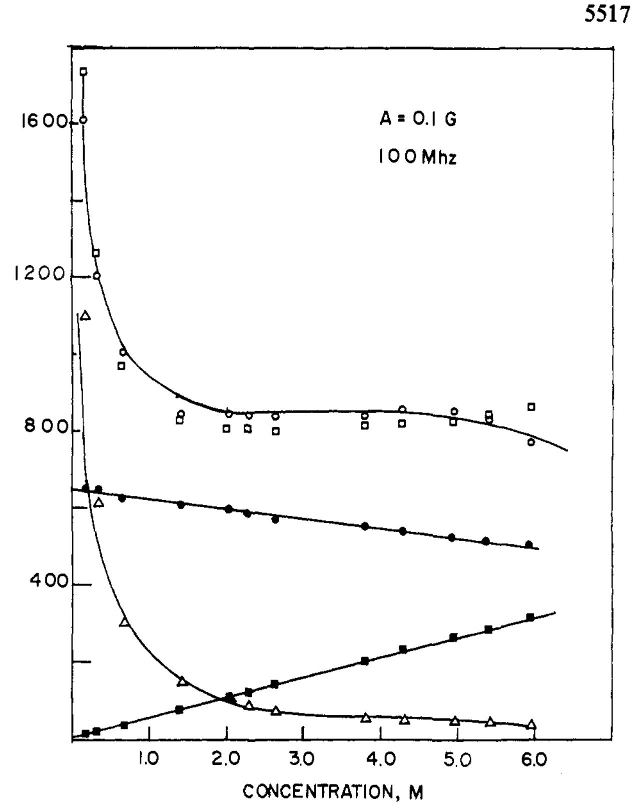

Figure 5. Experimental and theoretical contributions to the transverse relaxation time at 100 MHz: (■) is the intermolecular term, (△) is the intramolecular scalar term, (●) is the intramolecular dipolar term, (○) is experimental $1/T_2$, (□) is theoretical $1/T_2$.

Both the dipolar and scalar terms can contribute to the intramolecular transverse relaxation times. The scalar term is small at high concentrations because of the small value of t_e but begins to increase when the concentration is reduced to 1 *M* and finally dominates the values of T_2 at concentrations below 0.1 *M*. A plot showing the contributions of the intermolecular term, the intramolecular dipolar and scalar terms, and the calculated and experimental values of $1/T_2$ at 100 MHz is shown in Figure 5. The dipolar contributions to the values of T_2 are analogous to the dipolar contributions to the values of T_1. The variation in T_2 with frequency is due to differences in the magnitude of the frequency-dependent dipolar term.

The match between experimental and theoretical values of T_1 and T_2 is good except at the highest concentrations of DBNO. In the most concentrated samples the experimental values of the relaxation times are larger than the theoretical values. This behavior might be explained by a variation in the kinetics of the spin-exchange reaction. Lower values of t_e would explain the increase in the experimental relaxation times. If clusters of radicals are formed in concentrated samples the spin-exchange reaction might involve a series of radicals in a cluster. Interactions of this type could lead to a decrease in the value of t_e.

Conclusions

The transverse and longitudinal relaxation times of the protons in the di-*tert*-butyl nitroxide radical can be analyzed in terms of the intermolecular and intramolecular electron–nuclear dipolar and scalar interactions. The longitudinal relaxation times can be accounted for solely in terms of the dipolar interaction while the scalar interaction makes a large contribution to the transverse relaxation times in the concentration region below about 1 M. The field dependence of the relaxation times is accounted for by the frequency-dependent dipolar term.

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Photochemical and Thermochemical Cis–Trans Isomerization of Azoxybenzene

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Abstract: A study has been made of thermal and photochemical isomerization of azoxybenzene. The activation energy of the cis to trans thermal isomerization was found to be 25 kcal/mol in 95% ethanol and 19 kcal/mol in heptane. Quantum yields for the photoisomerization were determined as 0.11 for trans to cis isomerization and 0.60 for cis to trans isomerization and were the same in heptane and ethanol and independent of the wavelength of the exciting light from 330 to 370 nm.

The cis–trans isomerization of stilbene and of azobenzene has been studied extensively; for the photochemical isomerization process, photostationary states have been established by direct irradiation,[1,2] as well as by photosensitization.[3,4] In the structurally similar compound, benzalaniline, photoisomerization has been observed only in flash photolysis.[5] The formation of *cis*-azoxybenzene from the trans isomer was first demonstrated in this laboratory.[6] We have now undertaken a study of the cis–trans isomerization of azoxybenzene.

Upon irradiation of *trans*-azoxybenzene (I) in solution, a number of reactions and equilibria need to be considered: (1) the photochemical cis–trans isomerization of I; (2) the thermochemical reconversion of the cis isomer (II) to I; (3) the Wallach rearrangement to form hydroxyazobenzene (III) [the reaction is known to proceed by acid catalysis to 4-hydroxyazobenzene (4-III), but irradiation of I is known to produce the 2 isomer (2-III)]; (4) cis–trans isomerizations of 2-III and also 4-III, if formed [fortunately, in both cases the cis compounds (2-IV and 4-IV) appear to be so *rapidly* reconverted to 2-III and 4-III that the cis compounds can be ignored safely]; (5) equilibrium of III with a keto form V (however, in view of the small amounts of III formed in the present work, the equilibria with V have had no bearing on the results).

With this multiplicity of competing reactions, we have decided to start our investigation with those reactions which appear to be the most rapid, and hence the least complicated, by these competitions. Consequently we have investigated the thermo- and photochemical cis–trans isomerization of azoxybenzene.

Results and Discussion

Thermal Reaction. The rate of the rearrangement of *cis*-azoxybenzene to its trans isomer was followed spectrophotometrically at 324 nm. The reaction is first order. Rate constants obtained at 5, 25 and 35° in ethanol, and at 5, 15 and 25° in heptane, are shown in Table I.

Table I. Rate Constants for the Thermal Cis → Trans Conversion of Azoxybenzene

Solvent	Temp, °C	k, sec^{-1} $\times 10^{-6}$	Std dev $\times 10^{-6}$
Ethanol	5	0.638	0.092
	25	14.6	0.37
	35	48.7	0.57
Heptane	5	15.65	0.73
	15	51.0	
	25	165	13

The most striking feature of these results is the tremendous difference in rates between solutions in ethanol and heptane; the difference in rate constants is almost one power of 10 at 25° and 25-fold at 5°. In azobenzene, the difference is reported to be threefold.[7] Activation parameters are shown in Table II.

Table II. Activation Parameters for the Thermal Cis → Trans Isomerization of Azoxybenzene

Solvent	E_a, kcal/mol	A, sec^{-1}
Ethanol	24.8	2.1×10^{13}
Heptane	19.4	2.4×10^{10}

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