

A STUDY OF THE CHARACTER OF MOLECULAR ROTATION OF NITROXYL RADICALS IN LIQUIDS BY ESR AND DIELECTRIC RELAXATION METHODS

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The possibility of combined application of ESR and dielectric relaxation methods in determining the character of molecular rotation of organic nitroxyl radicals in nonpolar liquids is studied for solutions of 2,2,6,6-tetramethyl-piperidine-N-oxide in decaline. Comparison of the two correlation times for rapid radical rotation obtained by both methods provides evidence for an essentially jump-like rotation of this radical.

Nitroxyl radicals have been widely used in the past years as spin probes for ESR study of the molecular motions in liquids [1-5].

In the rapid motion region of these radicals ($10^{-11} \lesssim \tau_2 \lesssim 10^{-9}$ s, τ_2 is the rotational correlation time of a spherical top radical which is the correlation time of a second rank tensor) their ESR spectra are known to be insensitive to the character of radical rotation and to depend only on its rate defined by τ_2^{-1} . The nature of radical reorientation may be elucidated, however, if one knows the ratio of the correlation times for two different rank tensors in molecule [6], for instance the ratio τ_1/τ_2 . As nitroxyl radicals have a constant dipole moment (i.e. first rank tensor) the time τ_1 can be determined from the dielectric relaxation measurements if dilute radical solution in a nonpolar medium. The aim of this work is a study of such a possibility.

Dilute solutions of 2,2,6,6-tetramethyl-piperidine-N-oxide (TEMPO) nitroxyl radical in decaline were chosen for this study since (1) TEMPO is nearly spherical in shape and therefore one may anticipate the anisotropy rotation effects to be small and (2) intermolecular interactions influencing the electric dipole correlation time may be neglected in dilute solution in nonpolar solvent.

Dielectric absorption measurements of radical solutions were performed in the X-band on a home built

instrument. A sample (about 0.2 cm^3) was placed along the symmetry axis of the cylindrical cavity H_{111} , which was in an arm of the double T-bridge. The imaginary part of the dielectric susceptibility (ϵ'') was separated using an active disbalance of the bridge [7] with simultaneous compensation of the frequency displacement by a frequency controlling system. The sensitivity of the instrument allowed to study TEMPO solutions down to 10^{-2} M. The instrument was calibrated with chromatographically pure solvents. The temperature was accurate to $\pm 1^\circ\text{C}$.

The macroscopic dielectric relaxation time τ_1^* was determined without measuring the absolute ϵ'' values by studying the temperature dependence of $\Delta\epsilon''$, the difference between the ϵ'' value of radical solution and that of the pure solvent. The maximum value of $\Delta\epsilon''$ corresponds to the condition $2\pi f\tau_1^* = 1$ (where f is the working X-band frequency, 9.15 GHz in our case). The observed dielectric relaxation time is known [8] to be practically coincident with the molecular correlation time τ_1 for a dilute solution of dipolar molecules in a nonpolar solvent. Therefore $\tau_1 = 1.8 \times 10^{-11}$ s at a temperature T_M , corresponding to a maximum of $\Delta\epsilon''$.

The ESR spectra of radical solutions at concentrations about 10^{-3} M were measured at a temperature T_M on a Varian E-4 spectrometer. The temperature was kept constant within $\pm 1^\circ\text{C}$. The rotational corre-

lation time τ_2 was calculated from experimental ESR line intensities and widths using an additional broadening technique [9] and the relation [10]

$$\tau_2 = 6.65 \Delta H_{+1} [(I_{+1}/I_{-1})^{1/2} - 1] \times 10^{-10} \text{ s}, \quad (1)$$

where ΔH_{+1} (in gauss) is the derivative line width of the low-field hyperfine component, I_{+1} , I_{-1} are the low-field and high-field line intensities. The τ_2 values thus determined were corrected for nonsecular terms in the spin hamiltonian as in ref. [11].

Fig. 1 shows the temperature dependence of $\Delta\epsilon''$. The maximum value of $\Delta\epsilon''$ corresponds to $T_M = -20 \pm 2^\circ\text{C}$. The maximum position is independent of radical concentration in the range $10^{-2} - 5 \times 10^{-2}$ M.

The τ_2 value determined from ESR spectra of radical solutions at atmospheric oxygen pressure (see fig. 2) by the procedure described is $(3.4 \pm 1) \times 10^{-11}$ s at a temperature T_M .

Thus the ratio of two correlation times τ_1/τ_2 amounts to 0.52 ± 0.2 .

According to theory [6] the ratio τ_1/τ_2 varies from 3 for a diffusional (continuous) rotation model to 1 for jump rotation if the average angle is rather large

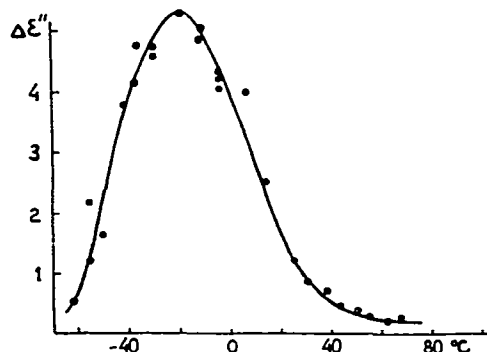


Fig. 1. Temperature dependence of $\Delta\epsilon''$ for TEMPO nitroxyl radical in decaline.

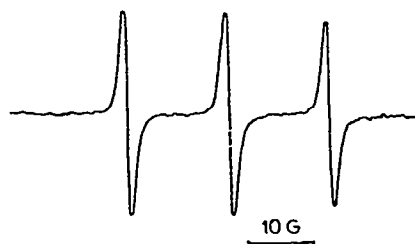


Fig. 2. ESR spectrum of TEMPO in decaline at atmospheric oxygen pressure at -20°C .

(no less than 120°). However as shown recently [12] the ratio τ_1/τ_2 may be less than unity for the same average jump angles if their dispersion is small relative to the average rotation angle as such.

We cannot claim that the ratio τ_1/τ_2 observed here is due to the above reason since the determination of τ_2 involved some approximations: (i) accurate values of the g and A tensors of the radical are unknown so that approximate values were taken when using eq. (1), and (ii) spherical top radical rotation was assumed.

The analysis of these approximations shows that although the lower ratio τ_1/τ_2 compared to unity is not quite certain, the conclusion, concerning the large angle of jump rotation of the radical under study seems to be reliable.

We note that this inference is in accordance with the conclusions drawn for TEMPO and its analogs from the ESR spectra in the slow motion region [1-5]*.

* The interpretation of the observed ratio τ_1/τ_2 is given here in terms of the generally accepted theory of stochastic rotation [6]. However, as kindly pointed out by the referee another explanation based on a model of slowly fluctuating torques is possible [5]. The conclusion that the rotation is not simple brownian remains valid.

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