qualitative theory, for it is still necessary to obtain these theoretical quantities for the *reaction path actually followed* in a given process. Calculating these results over higher energy paths can and has led to prediction of a different stereochemical route than that favored experimentally; clearly, only energy comparisons for the minimum-energy paths available to each rotational mode are of experimental consequence. Examples of the importance of this point can be found in the present C_4H_6 calculations, which have indicated that the actual rotation in this isomerization occurs only over a very narrow range of the terminal CC bond distance, that is, for structures with a considerably expanded cyclobutene ring. The effect of taking into account these details of the reaction path is to cause a change in the designation of the critical MO for the 90° structure in the thermochemical process (albeit no change in the prediction of the preferred rotational mode) and, more significantly, to eliminate all critical species for the photochemically induced transformation. Thus, the qualitative theory is seen to be somewhat ambiguous with regard to predictions of the preferred photochemical rotational mode, indicating that the total energy difference between the potential maxima of dis- and conrotatory processes is much smaller in absolute magnitude in the reaction involving the lowest excited states of these systems than for their ground states.

In summary, there seem to be two rather well-defined areas in which one can expect to find that conservation of orbital symmetry is violated. In the first area, exceptions might occur because one product is much more stable than the other; staggered energy levels could well lead to a situation in which the total energy difference does not take its sign from that of the critical orbital energy term. In the second case, exceptions might be expected to arise because a change in electronic configuration occurs as one product is converted into its prerotation conformation; clearly, such situations are not so much exceptions to the qualitative theory as they are evidence of its incorrect application. Acquiring an accurate picture of the reaction mechanisms operative in each type of electrocyclic transformation should all but eliminate such pitfalls, and this objective should therefore be the goal of quantum mechanical calculations in the near future.

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Studies on Diffusion and Diffusion-Controlled Reactions Involving Alkyl Radicals in Solution

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Abstract: The method of photochemical space intermittency (PCSI) has been used to measure diffusion coefficients of propyl, pentyl, dodecyl, and octadecyl radicals in solution. The measured diffusion coefficients are smaller than would have been predicted for the parent hydrocarbons. In combination with the Smoluchowski equation, these diffusion coefficients yield calculated rate constants for radical combination–disproportionation which are in good agreement with experimental values for all but the octadecyl radical. The unusually small diffusion coefficient of the pentyl radical indicates that a certain portion of its lifetime is spent in a state such that its translational mobility is inhibited.

Diffusion coefficients of very reactive species are difficult to determine by classical methods because of the very short lifetimes involved. In fact, it was not until a few years ago that Noyes and his coworkers carried out diffusion measurements on the reactive iodine atom in solution using the method known as photochemical space intermittency (PCSI).[2,3] Apparently the only other reported use of the PCSI method is that of Davies and North,[4] who performed some diffusion measurements on the polystyryl radical in solution.

The diffusive behavior of free radicals in solution is obviously of interest to kineticists concerned with the rates of supposedly diffusion-controlled processes. For instance, conclusions about whether or not certain radical–radical reactions are really diffusion controlled have been necessarily based upon the assumption that the frictional force of a radical species may be calculated using Stokes'[5] law or that a free radical, R·, and its parent, RH, have the same diffusion coefficient in a given medium.[6] It is desirable to test these ideas experimentally.

The PCSI method involves the photochemical production of free radicals in a spatially nonhomogeneous fashion. This may be accomplished by irradiating the reaction mixture through a space-intermittency pattern so that illuminated and dark regions exist in a regular

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[1] (a) NDEA fellow 1966–1969; (b) NASA fellow 1965–1966, NDEA fellow 1966–1969.

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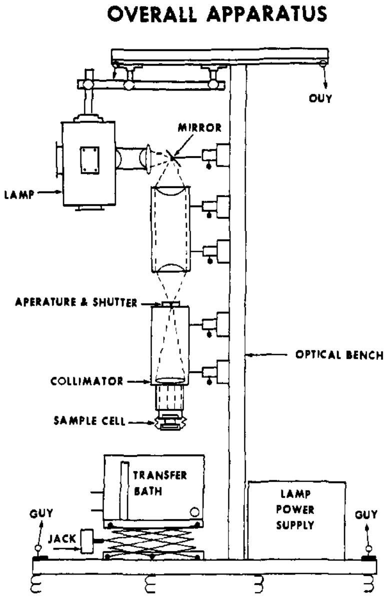

Figure 1. Diagram of photochemical space intermittency apparatus.

geometric array through the solution. If a method can be found for monitoring the average steady-state concentration of radicals which is insensitive to the spatial distribution of radicals, then the diffusion coefficients of these species can, in principle, be measured.

The present study utilized a "leopard" space-intermittency pattern of the type used by Levison and Noyes.[3] Free radicals were produced and monitored by means of the photoinitiated radical-chain reaction between triethyl phosphite and various thiols.[6] Although no diffusion data for alkanes in cyclohexane appear to be available, this solvent does possess the advantage of being chemically inert in the present application, and it was used for all of the studies reported here.

In order to perform a complete analysis of the PCSI data to obtain diffusion coefficients, it is necessary to know the specific rate constants, k_t, for the termination step in each monitor reaction. In the present case the termination reactions are the corresponding alkyl radical–alkyl radical combination–disproportionation processes. The use of the triethyl phosphite–thiol reaction to obtain k_t values has been demonstrated previously[6,7] by the use of time-intermittent illumination. It will be recognized that the k_t values obtained from time-intermittency studies actually serve the twofold purpose of making possible a complete analysis of the diffusion data as well as providing an immediate testing ground to determine whether measured diffusion coefficients in combination with the Smoluchowski equation reproduce the measured values of k_t. Although the k_t measurements and the diffusion measurements were carried out as separate projects, they are being discussed here together because of their intimate interconnection.

Experimental Section

A description of the apparatus used for the rotating sector experiments and a discussion of the techniques used for individual runs have been given in previous publications.[6,7] An overall view of the apparatus used for diffusion measurements is shown in Figure 1. One of the primary requirements of the PCSI experiment is that the incident light beam be sufficiently collimated so that the image of the intermittency pattern is transmitted in an essentially undistorted fashion through the solution. It seems that a necessary prerequisite is a lamp which approximates a point source as closely as possible.[8] The lamp finally chosen for this work was a high-pressure short-arc mercury lamp rated at 100 W (Illumination Industries Inc.). The arc length of these lamps is less than 1 mm, and photographic tests showed that the image of the intermittency pattern is essentially undistorted in its passage through a layer of solution 2.5 cm thick.

The configuration of the light path shown in Figure 1 indicates that the light beam is directed downward, passing through the intermittency pattern and entering the reaction cell from the top. In this way it was thought that convection currents would be minimized.

The optical system utilized glass lenses; the vertical reflection was accomplished using a first surface polished aluminum mirror (Gaertner Scientific Corp.). A Corning No. 5840 glass filter was inserted into the light beam just below the mirror. This filter has a high-wavelength cutoff at about 3960 Å. The reaction cells were made of Pyrex so that light below about 3200 Å is not transmitted. This light-filtration system has been used previously to isolate the 3660-Å mercury emission, but it was found to be unsatisfactory with short-arc lamps as the light source. Background continuous emission is relatively intense with these short-arc lamps, so it was necessary also to insert an interference filter (Bausch and Lomb Co.) having a peak transmission at 3660 Å. The filter was inserted after the last collimating lens just preceding the intermittency pattern. Light intensities were monitored using a photovoltaic cell placed directly beneath the reaction cell.

The space-intermittency patterns were prepared by photoetching a thin silver mirror which has been deposited on an optically plane quartz disk 1.5 in. in diameter. Another optically plane quartz disk was placed over the pattern and the two pieces were sealed together using a waterproof cement. This work was performed by Buckbee-Mears, Inc., St. Paul, Minn. The present studies utilized a so-called leopard pattern, which consists of an array of light-transmitting spots, each spot having six nearest neighbors.[3] The center of each spot is three spot diameters distant from the center of each nearest neighbor. The negative used in the photoetching was supplied by Professor R. M. Noyes of the University of Oregon.

The reaction cell used in the PCSI experiments was cylindrical, with optically plane Pyrex windows and a light path 2.5 cm long. The cell was attached to the side of a piece of 15-mm Pyrex tubing which was about 4 in. long, closed at the bottom and with a 19/38 ₸ joint at the top. The tubing leading from the cell to the 15-mm Pyrex tube was about 2 in. long. A 1-in. section of this tubing adjacent to the cell was a 0.5-mm. i.d. capillary, and it was bent at an angle such that its end was above the top face of the reaction cell during a reaction. Thus, when the cell was filled the capillary section was also filled, but the volume of solution which it contained was negligibly small.

All of the rate experiments were carried out at 25 ± 0.05°. Thermostated water was circulated by pumping into the Plexiglass transfer bath and then using gravity drainage back to the reservoir. The height of the transfer bath could be adjusted by use of a jack. With this system there were no moving parts on the platform upon which the PCSI apparatus was mounted. The platform itself was mounted on a set of springs, and foam rubber shock absorbers were placed at the four corners in order to damp out spurious mechanical vibrations.

In preparing for a PSCI run, the reactants were measured into volumetric flasks with final dilution to the mark with solvent. About 7.5 ml of the solution was then introduced into the side tube of the reaction apparatus. An adapter and stopcock were attached to the ground-glass joint at the top of the tube so that the apparatus could be connected to a vacuum line. The solution was out-gassed using at least four freeze–thaw cycles, and after warming to room temperature, the solution was transferred to the reaction cell. The cell was attached to the apparatus at the position indicated in Figure 1 and was then irradiated for the desired length of time using either full illumination or illumination through a spot pattern.

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(8) R. M. Noyes, *ibid.*, **69**, 3182 (1965).

All of the thiols were purchased from Aldrich Chemical Co. and were purified by distillation in a nitrogen atmosphere; vacuum distillations were used for 1-dodecanethiol and 1-octadecanethiol. Triethyl phosphite was distilled twice under vacuum through a 30-in. Vigreux column and was stored in a glass-stoppered vessel which was kept inside of a dessicator that had been painted black. Azocyanocyclohexane (ACC) and 2 2′-azobisisobutyronitrile (ABN) were purified by recrystallization twice from ethanol followed by vacuum drying overnight.

Reaction rates were measured by the rate of disappearance of thiols. Potentiometric titrations with the mercuric ion were used to determine thiol concentrations.[9] In the rotating-sector experiments light intensities were measured using the potassium ferrioxalate actinometer[10] and rates of initiation could then be determined from the known extinction coefficient of ABN at 366 nm[11] and from the known initiator efficiency[12] of this azo compound. Since overall rate constants for the 1-propanethiol–triethyl phosphite reaction[7] and the 1-octadecanethiol–triethyl phosphite reaction were known when the PCSI experiments were begun, these were used to determine rates of initiation for all rate experiments carried out on the PCSI apparatus.

Results and Discussion

All of the rotating-sector experiments were done using ABN as the photoinitiator, and no problems due to the thermal decomposition of this compound have been observed. With the PCSI experiments, however, the space-intermittency masks pass only about 10% of the incident light so thermal initiation exerts a noticeable perturbation on the results. A correction theory was worked out so that ABN may be used for PSCI work, but a preferable approach and the one adopted here is to use ACC as the photoinitiator since its rate of thermal decomposition at 25° is only about 0.025 that of ABN.[13] The triethyl phosphite–thiol reaction is thought to occur *via* the following mechanism.

$$\text{ACC (or ABN)} \xrightarrow{h\nu} 2\text{A}\cdot + \text{N}_2 \tag{1}$$

$$\text{A}\cdot + \text{RSH} \longrightarrow \text{AH} + \text{RS}\cdot \tag{2}$$

$$\text{RS}\cdot + \text{P(OEt)}_3 \longrightarrow \text{R}\cdot + \text{SP(OEt)}_3 \tag{3}$$

$$\text{R}\cdot + \text{RSH} \xrightarrow{k_p} \text{RH} + \text{RS}\cdot \tag{4}$$

$$2\text{R}\cdot \xrightarrow{k_t} \text{products} \tag{5}$$

The rate of thiol disappearance in step 2 is negligible compared to that in step 4 for this long-chain reaction. Also, in a given experiment a negligible fraction of the photoinitiator is lost, so that under steady-state conditions and using temporally and spatially uniform illumination

$$\frac{1}{t}\ln\frac{[\text{RSH}]_0}{[\text{RSH}]} = k_p[k_t/\phi q]^{-1/2} \tag{6}$$

In this equation q is the rate of light absorption and ϕ is the fraction of free initiator radicals produced per quantum of light absorbed.

The specific rate constants k_p and k_t have already been measured for the 1-propanethiol system.[7] They are 2.9×10^6 and 1.7×10^9 M^{-1} sec^{-1}, respectively. For the homologous series of 1-alkyl radicals one would not expect k_p to change appreciable from one member to the next; however, rotating-sector experiments were carried out on the 1-octadecanethiol system to see if this expectation is correct. The data are shown in Figure 2, from which one finds τ = 9.8 sec for $\phi q = 6.3 \times 10^{-12}$ M sec^{-1}. This yields $k_t = 4.1 \times 10^8$ M^{-1} sec^{-1}. Experiments using steady illumination showed that $k_p/k_t^{1/2}$ = 142 $M^{-1/2}$ sec$^{-1/2}$ for this system, so that $k_p = 2.9 \times 10^6$ M^{-1} sec^{-1}. The exact agreement between propyl and octadecyl systems is, of course, accidental, but does indicate that k_p has no appreciable dependence on chain length in this homologous series.

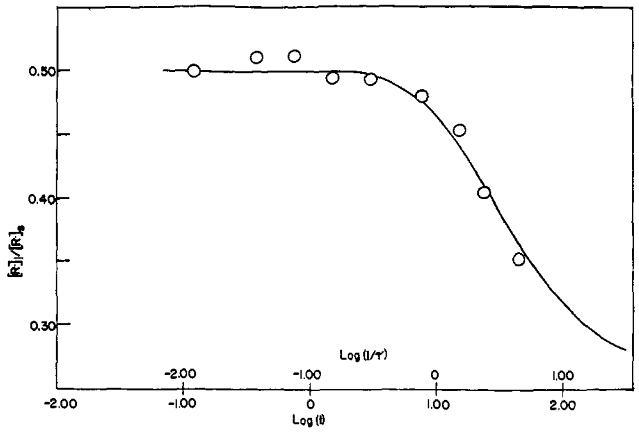

Figure 2. Graph of the ratio of average octadecyl radical concentrations during intermittent $[\text{R}]_\text{i}$ and steady $[\text{R}\cdot]_\text{s}$ illumination *vs.* log t/τ (solid curve) and log t (experimental points).

Table I gives a summary of rate experiments carried out using temporally and spatially uniform illumination on the four systems studied here.

Table I. Values of $k_p/k_t^{1/2}$ and k_t for Four Alkyl Radical Systems in Cyclohexane

Radical	$k_p/k_t^{1/2}$, $M^{-1/2}$ sec$^{-1/2}$	k_t, M^{-1} sec^{-1} $\times 10^{-8}$
1-Propyl[a,b]	68.8[d]	17[d]
1-Pentyl[c]	202	2.1
1-Dodecyl[c]	113	6.8
1-Octadecyl[a]	142	4.1

[a] k_t found by rotating-sector work. [b] See ref 7. [c] k_t calculated from $k_p/k_t^{1/2}$ assuming $k_p = 2.9 \times 10^6$ M^{-1} sec^{-1}. [d] The overall precision in k_p and k_t values is estimated to be ±10 and ±25%, respectively, of the reported values.

The decrease in k_t with increasing chain length which is found for the propyl, dodecyl, and octadecyl systems is to be expected for diffusion-controlled reactions. The deviation of the pentyl radical from this pattern represents an interesting case which we shall consider in more detail after presenting the diffusion data.

For PCSI experiments the leopard space-intermittency patterns were used. For these patterns it is convenient to follow Noyes[14] and define

$$\rho = (4\phi q k_t/D^2)^{1/4} r \tag{7}$$

and

$$\gamma = (k_t/\phi q)^{1/2}[\text{R}\cdot] \tag{8}$$

where D is the diffusion coefficient and r is the distance from the center of a spot. When the distance away

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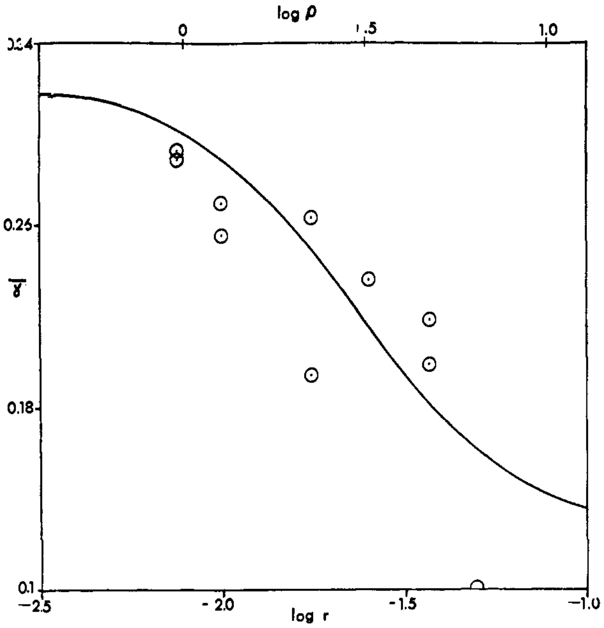

Figure 3. Graph of $\bar{\gamma}$ *vs.* log r (lower scale and experimental points) and *vs.* log ρ (upper scale and solid curve) for the propyl radical system.

from the center of a spot is equal to the spot radius, then $r = r_0$ and the corresponding value of ρ is ρ_0. Using numerical integrations, γ has been obtained as a function of ρ so that one may obtain $\bar{\gamma}$, the spatially averaged value of γ by using

$$\bar{\gamma} = 2\pi \int_0^{3\rho_0} \gamma\rho \, d\rho / 9\pi\rho_0^2 \qquad (9)$$

Values of $\bar{\gamma}$ as a function of ρ_0 may be worked out using Noyes' tabulation.[14] When a spot pattern is used, one may experimentally obtain

$$\frac{1}{t} \ln \frac{[\mathrm{RSH}]_0}{[\mathrm{RSH}]_t} = k_p \bar{\gamma} (k_t/\phi q)^{-1/2} \qquad (10)$$

Thus, by a comparison of results for spatially uniform illumination and illumination through a spot pattern (eq 6 and 10), $\bar{\gamma}$ is seen to be experimentally accessible for any value of r_0 which one chooses.

PCSI experiments were carried out for the four alkyl radical systems mentioned in Table I. Typical data in the form of $\bar{\gamma}$ *vs.* log r for the propyl radical system are shown in Figure 3. The solid curve in this figure is a graph of $\bar{\gamma}$ *vs.* log ρ. Its shape is fixed by theory and the numerical calculations mentioned above; however, the entire curve may be adjusted by horizontal translation to give the best fit with the experimental data. In practice it was found that the placement of the solid curve was accomplished more objectively if all the data for a given spot size were averaged. For the propyl radical it may be seen from the graph that r_1, the value of r corresponding to $\rho = 1$, is 0.0078 cm.

The measured value of ϕq for the propyl system was 2.6×10^{-12} M sec^{-1}, and k_t for this system is given in Table I. The diffusion coefficient calculated from eq 7 is 8.0×10^{-6} cm^2 sec^{-1}. A similar treatment of the data for the pentyl, dodecyl, and octadecyl systems yields the results of Table II.

Table II. Values of r_1, ϕq, and the Resulting Diffusion Coefficients for Four Alkyl Radicals in Cyclohexane

Radical	r_1, cm	ϕq, M sec^{-1} × 10^{12}	D,[a] cm^2 sec^{-1} × 10^6
1-Propyl	0.0078	2.6	8.0 (24.6)[b]
1-Pentyl	0.0035	4.8	0.8 (22.1)
1-Dodecyl	0.0044	2.6	1.6 (10.8)
1-Octadecyl	0.0071	1.8	2.7 (7.8)

[a] The estimated relative error in D is ±60% of the reported value. [b] Diffusion coefficients in parentheses were calculated according to the methods of ref 16.

As expected, the diffusion coefficients for dodecyl and octadecyl radicals are the same within experimental error. Furthermore, the propyl radical diffusion coefficient is between three and four times as large as those found for the dodecyl and octadecyl radicals, and this ratio is very close to that predicted using the Kirkwood formula for translational diffusion.[15] On the other hand, the diffusion data obtained for the pentyl radical are very difficult to accommodate within the framework of the other three systems.

The calculated diffusion coefficients presented in Table II are made using the Kirkwood formula in exactly the same way as was done previously in calculations of the diffusion coefficients of alkanes.[16] These previous comparisons between theory and experiment for alkane diffusion showed that, if anything, the theory underestimated D but that generally the agreement between theory and experiment was reasonably good. One of the most striking observations of the present study is that, in every case, the theory grossly overestimates the diffusion coefficient even if one takes into account the relatively large uncertainty in the experimental results. Unfortunately, there appear to be no measurements of alkane diffusion coefficients in cyclohexane, thus precluding a comparison of results for alkanes and alkyl radicals under identical conditions. In view of the rather accurate predictions which the theory has made for other solvents, it would be surprising if the situation were appreciably different in cyclohexane. In this context, therefore, the diffusion coefficients found in this study are considered to be somewhat smaller than would have been predicted.

One of the original motivations for this work was in connection with studies of diffusion-controlled radical–radical reactions. In Table III are presented some specific rate constants for the radical–radical reaction calculated from the Smoluchowski equation using the measured diffusion coefficients and assuming that the encounter radius is equal to the root-mean-square

Table III. Calculated Alkyl Radical Recombination Rate Constants Using Experimental Diffusion Data

Radical	$\langle l^2 \rangle^{1/2}$, cm × 10^8	k, M^{-1} sec^{-1} × 10^{-8}
1-Propyl	2.8	18 (17)[a]
1-Pentyl	4.4	2.7 (2.1)
1-Dodecyl	11	12 (6.8)
1-Octadecyl	15	31 (4.1)

[a] Experimental results are in parentheses.

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(15) For a recent review on the dynamics of polymeric species in solution, see M. Fixman and W. H. Stockmayer, *Annu. Rev. Phys. Chem.*, **21**, 407 (1970).

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end-to-end distance of the reacting radical, $\langle l^2\rangle^{1/2}$. Comparing calculated and experimental results, one finds that the only serious deviation is where one would expect to find it, namely with the octadecyl radical. The remaining rate constants show agreement within experimental error. There are two points, concerning these results which must be discussed.

First, one notices that the deviation between theory and experiment for the octadecyl radical may be an indication that such long-chain species do not react at every encounter. An alternative interpretation is that an encounter between long-chain species involves a certain amount of interpenetration before reaction can occur so that the effective encounter diameter is actually less than $\langle l^2\rangle^{1/2}$. The present experiments are not able to provide a distinction between these two interpretations.

The second notable point concerning the data of Table III has to do with the results for the pentyl radical. The value of k_t for this radical is unusually small, but so is its measured diffusion coefficient; hence, one finds good agreement between experimental and calculated values of k_t. Since both k_t and D are determined by making rate measurements on the same monitor reaction, it was decided to review this reaction to try to determine whether or not it contained a source of error for these measurements. Since the results for the other three radicals seemed to be in reasonable accord with expectations, and since triethyl phosphite is a reagent common to all of the reactions, one tries to find a singularity associated with the thiol or with the corresponding thiyl or alkyl radical. It appears that the most likely point at which one of these species could be trapped so that translational motion might be inhibited would be in connection with eq 3. Here the pentyl radical may exist as a caged pair with $SP(OEt)_3$ and undergo a number of nonrandom diffusive displacements before moving into the bulk solution. Presumably, propyl radicals are small enough to enjoy more efficient escape and dodecyl and octadecyl are large enough so that only a small fraction of the chain molecule is ever trapped. Thus, the results of these studies, while useful in interpreting the diffusion-controlled nature of k_t for some radicals, may not be as generally applicable as one would like. These results also indicate the need for devising systems in which radicals are produced in a kinetically free state if solution properties of these reactive species are to be studied.

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On the Flexibility of Hydrocarbon Chains in Lipid Bilayers[1]

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Abstract: The spin label technique is used to investigate the flexibility of the hydrocarbon chains of a smectic phase with bilayer structure. The experimental data, especially the temperature dependence of the flexibility, can be explained in terms of a phenomenological theory which is based on the mathematical formalism of the rotational isomeric model. This approach leads to conclusions about the apparent configurational entropy per methylene group which are consistent with calorimetric data.

Bilayer structures play an important role in biological membranes, and detailed knowledge of the way bilayer lipids are organized will eventually lead to an understanding of membrane properties.[2,3] One intriguing aspect of the rather complex situation is the configuration of the hydrocarbon chains in the lipid bilayer. In a previous publication we have shown how the spin label technique can be employed in solving this question.[4] Briefly, our investigation of smectic liquid crystals and phospholipid dispersions has resulted in the following findings. (1) The lipid bilayers are highly fluid in the sense that the hydrocarbon chains are rotating rapidly ($>10^8$ cps) around their long molecular axes. (2) The hydrocarbon chains are neither coiled nor completely extended; instead, the experiments reveal a high degree of order of the hydrocarbon chain in the region adjacent to the hydrophilic environment, which decays exponentially when going into the hydrophobic interior. This decrease of the degree of order is due to the intrinsic flexibility of the hydrocarbon chains. We have now extended our earlier measurements to determine the temperature dependence of this flexibility. Furthermore, we wish to describe how the experimental data can be explained to a first approximation, by applying a phenomenological theory using the formalism of the rotational isomeric model.[5–7] This approach will also enable us to calculate the apparent configurational entropy per

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