Table VI

substituent type	main cyclopropane MO involved	C_1C_2 vicinal	C_2C_3 distal	favored substituent conformation
π-acceptor	3e′(R) π-type	longer	shorter	bisected
π-donor	4e′(L) π′-type	longer	shorter	perpendicular
σ-acceptor	1e″(L)	shorter	longer	
σ-donor	1e″(L)	longer	shorter	

π-interactions can be regarded as perturbing effects and have been overemphasized in the past, especially for fluorine substituents which function as σ-acceptors and not as π-donors.

As has long been appreciated,[4,5,11-17] cyclopropyl is a fairly strong π-donor and is stabilized by π-acceptor substituents but only in bisected conformations. Cyclopropyl is less effective as a π-acceptor, but strong π-donor substituents lead to some stabilization by interaction with the 4e′ (L) LUMO, the main acceptor orbital. This orbital is a π′-acceptor, as defined above, and favors orientations of substituent lone-pair orbitals in the C_s C_3H_5X plane. Thus, cyclopropylamine prefers trans and cyclopropanol skew conformations. Contrary to earlier interpretations, the $1a'_2$ Walsh orbital is not of major importance (with the possible exception of negatively charged substituents, e.g., O^-, and bisected CH_2^-).[22]

Although any given substituent will interact significantly with several cyclopropane orbitals, it is useful to identify the principle effects. These can be used in a simple way to predict changes in bond lengths and favored conformations, as summarized in Table VI.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and was facilitated by the cooperation of the Regionales Rechenzentrum Erlangen.

Registry No. $(CH_3)_2CH_2$, 74-98-6; *i*-PrLi, 1888-75-1; *i*-PrBeH, 90823-09-9; *i*-$PrBH_2$, 17643-29-7; $(CH_3)_3CH$, 75-28-5; *i*-$PrNH_2$, 75-31-0; *i*-PrOH, 67-63-0; *i*-PrF, 420-26-8; cyclopropyllithium, 3002-94-6; cyclopropylhydroberyllium, 84064-91-5; cyclopropylborane, 72507-58-5; methylcyclopropane, 594-11-6; cyclopropanamine, 765-30-0; cyclopropanol, 16545-68-9; fluorocyclopropane, 1959-79-1.

Supplementary Material Available: Complete 4-31G optimized geometries and coordinates for the cyclopropyl and 2-propyl derivatives (18 pages). Ordering information is given on any current masthead page.

Transient EPR and Magnetophotoselection in the Photolytic Formation of a Trimethylenemethane Biradical

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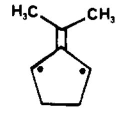
Abstract: The transient EPR response of the triplet biradical 2-isopropylidenecyclopenta-1,3-diyl accompanying its production by pulsed laser photolysis at 337 nm reveals that the biradical is born predominantly in the T_z zero-field substate and the coupling constant D is positive. Magnetophotoselection experiments demonstrate that the electric dipole transition moment in the diazene precursor is parallel to the in-plane magnetic axis which yields the smallest of the three high-field spin–spin splittings. Symmetry considerations bearing on the results are presented.

Processes which carry a molecule between its singlet and triplet manifolds are usually state selective; i.e., crossing from a given singlet state to only one of the three triplet sublevels usually predominates. Many instances of the phenomenon have been uncovered in studies of the population and depopulation of photoexcited triplets. In solid solutions of some aromatic molecules in crystalline hosts such as fluorene or benzoic acid, state selectivity is preserved to temperatures just below the melting point of the hosts. CIDEP phenomena in liquids demonstrate the persistence of the selectivity in fluid media.

In contrast to the many studies of triplet–singlet interconversions in which a single molecular species evolves with no change in molecular composition among states accessible to it, there have been to our knowledge only a few reported instances of state selectivity in chemical processes in which a singlet precursor is irreversibly disrupted to yield a triplet product.[1,2]

In each of the cited cases the triplet product is born predominantly in only one of its zero-field eigenstates. The eigenstates in an external magnetic field are superpositions of the zero-field ones. Their populations at instant of birth are determined by their composition. We report here our studies of the formation of the biradical **1** by photolysis of the diazene **2**.



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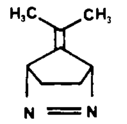

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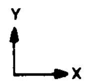

Experimental Section

Transient Experiments. The diazene **2** in rigid isotropic solution in methyltetrahydrofuran or octafluorotoluene was photolyzed at 77 K in the cavity of an X-band EPR spectrometer by light from a nitrogen laser, λ 337 nm, pulse duration 10 ns, pulse energy less than 1 mJ.

The transient responses at the fields at which the conventional CW spectra (derivative of absorption with respect to magnetic field vs.

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(1) Doetschman, D. C. *J. Phys. Chem.* **1976**, *80*, 2167.

(2) Chisholm, W. P.; Weissman, S. I.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 7104.

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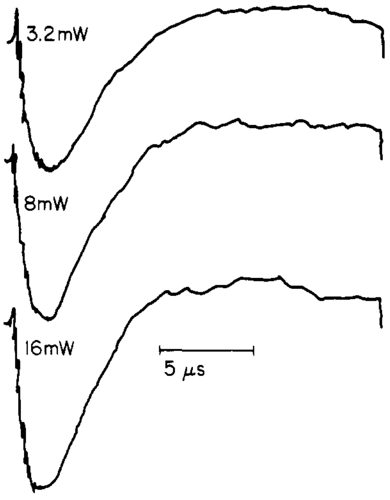


Figure 1. Typical transient EPR accompanying pulsed photolysis.

magnetic field) have their peaks were obtained by the direct method in which no field modulation is used and the output of the detecting diode is recorded in a transient digitizer.[3]

The spectrometer was tuned to respond to the absorptive component of magnetization. The amplified signal was digitized in a Biomation 8100 transient digitizer operating at a sampling rate of 100 MHz. Each digitized transient was transferred to a PDP 11-10 computer where several hundred repetitions were averaged. The laser flash produces a small field-independent transient response which was subtracted in the averaging process. The sample was moved as required to expose fresh regions to the light. Frequent monitoring of the CW signal ensured that we obtained data in a regime in which the number of biradical molecules produced per pulse remained almost constant.

Magnetophotoselection Experiments. The experiments were performed at 77 K in rigid solution in methyltetrahydrofuran. The appropriate polarized component of the laser light was selected by a large Wollaston prism (a gift from the late Arthur L. Hughes, who used it in his experiments on photoelectricity more than 60 years ago). The spectra for both $\vec{E} \parallel \vec{B}$ and $\vec{E} \perp \vec{B}$ ($\vec{E}$ is the electric vector of the light, $\vec{B}$ the static magnetic field) were obtained after only one irradiation. The vertical sample tube was irradiated with horizontally polarized light; rotation of the tube about its axis controlled the relation between the direction of $\vec{E}$ imprinted in the sample and $\vec{B}$. To make doubly sure that we had the correct polarizations we carried out the photolysis with $\vec{E}$ vertical; the spectrum was identical with the one obtained after appropriate rotation of the sample tube after photolysis with $\vec{E}$ horizontal and was independent of rotation around the vertical axis.

Results and Discussion

The transient results are easily described: at each of the three low-field peaks the transient response is absorptive; at each of the high-field ones, emissive. Except for the switch in sign between low- and high-field responses, the shape of the transient is almost independent of field: a rapid rise (some tenths of a microsecond) followed by monotonic decay with characteristic time of several microseconds (Figure 1). No oscillatory transient nutations were observed. The absence of oscillations, although it is symptomatic of several interesting possibilities, shall not be discussed in this paper. It is only the initial sense of the transient, absorptive (A) or emissive (E), which we use in determining the sign of the spin–spin coupling constant and which magnetic substate of the biradical is initially populated. As we demonstrate below, the emissive absorptive pattern leads to an unambiguous assignment.

We use the standard spin Hamiltonian for analysis of the experimental results: $\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + \vec{B}\cdot\vec{S}$ where D, E, and B are all in magnetic field units and x, y, z are molecule-fixed coordinate axes along the principal directions of the spin–spin interaction. (For the purists who demand a trace less spin–spin tensor we could add the constant term $-D/3(S_x^2 + S_y^2 + S_z^2) = -2D/3$ which does not affect the energy intervals.) We adopt the usual convention that the molecular z axis is the one which yields maximum splitting when the external field B is parallel to it ($|B| > |D|$). The x and y axes are arbitrarily chosen so that D and E have the same sign. Once these conventions are adopted the zero-field energies E_x, E_y, and E_z are ordered $E_y > E_x > E_z$ for $D > 0$ and $E_z > E_x > E_y$ for $D < 0$. At high field the outermost peaks are labeled Z, the innermost ones X, and the intermediate ones Y.

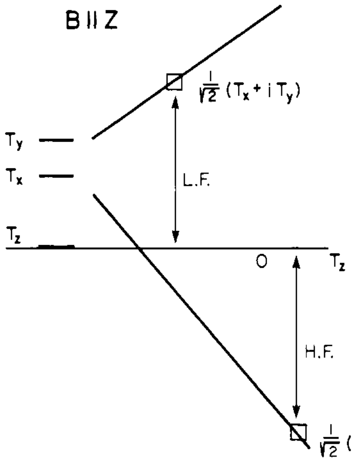


Figure 2. Energy vs. magnetic field for $B \parallel Z$. Excess population if T_x and/or T_y are initially populated, HF; if T_z is initially populated, LF.

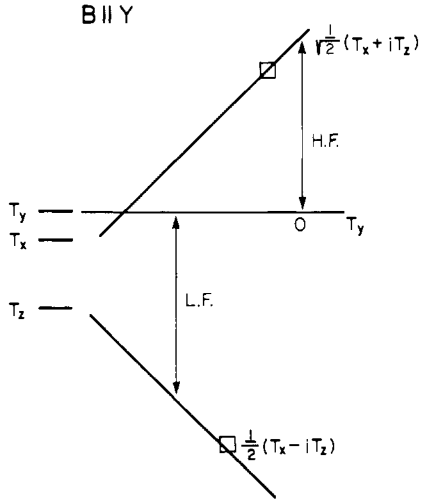
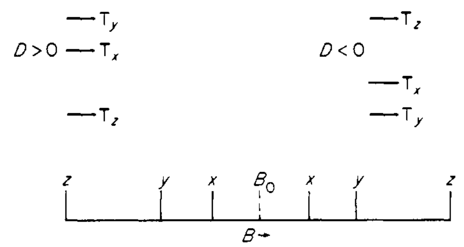


Figure 3. Energy vs. magnetic field for $B \parallel Y$.: Excess population if T_z and/or T_x are initially populated, HF; if T_y is initially populated, LF.



The Z peaks appear at $B_0 \pm D$, the Y peaks at $B_0 \pm (D + 3E)/2$, and the X peaks at $B_0 \pm (D - 3E)/2$.

We now describe how the sign of D and which zero-field triplet substate is initially populated are determined from the emissive–absorptive character of the transients. For $D > 0$ the dependence of energy on magnetic field and the composition of the states at high field for the three canonical orientations is shown in Figures 2–4.

We calculate the emissive–absorptive character for the six possibilities, $D > 0$, T_x, T_y, or T_z populated, and $D < 0$, T_x, T_y, or T_z populated, and present the results in Chart I.

The assignment is unambiguous because labeling the X, Y, and Z peaks is unambiguous; perhaps they should have been labeled I (inner), M (middle), and O (outer).

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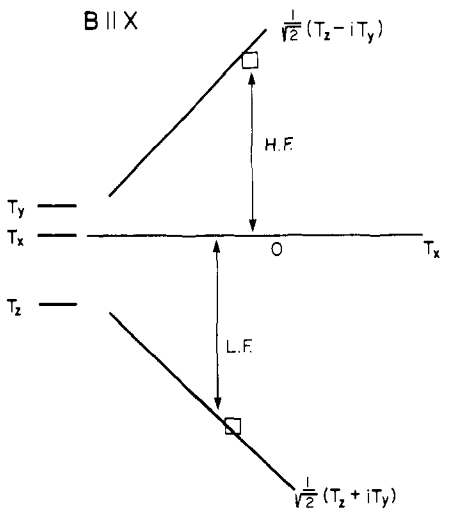

Figure 4. Energy vs. magnetic field for $B \parallel X$. Excess population if T_z and/or T_y are initially populated, HF; if T_x is initially populated, LF.

Chart I

	Z	Y	X
LF	A	A	A
HF	E	E	E

T_z populated

	Z	Y	X
LF	E	A	E
HF	A	E	A

T_x populated

	Z	Y	X
LF	E	E	A
HF	A	A	E

T_y populated

	Z	Y	X
LF	E	E	E
HF	A	A	A

T_z populated

	Z	Y	X
LF	A	E	A
HF	E	A	E

T_x populated

	Z	Y	X
LF	A	A	E
HF	E	E	A

T_y populated

Although we have six physically realizable situations, we could have written eight possibilities which fulfill the requirement that in each pair of peaks X, Y, or Z one is always emissive and the other absorptive. The nonrealized pairs are

	Z	Y	X
LF	E	A	A
HF	A	E	E

and

	Z	Y	X
LF	A	E	E
HF	E	A	A

To our knowledge these patterns have not been found in triplets that have been formed by intersystem crossing from a singlet state. They have, however, been observed when a triplet is formed from one member of a radical pair; in this situation the $M_s = 0$ state is predominantly populated at all orientations in the external field.[4]

In the foregoing discussion we have treated the ideal case in which at each setting of the magnetic field only those molecules one of whose principal axes is nearly parallel to the field contribute to the transient. The assumption is valid only for the Z peaks in an isotropic distribution. For molecules with $E = 0$ in addition to those whose xy axes are parallel to the field ones whose z axes are tilted about 35° from the field f contribute to the signal. Nevertheless, owing to the fact that the initial population differences are maximum at the canonical orientations, the contributions from the noncanonical orientations do not obscure the sense of the transients contributed by the canonical orientations. This effect is nicely demonstrated in the behavior of transients from triplet hexahelicene in random orientation where the sign of the transient switches from emissive to absorptive as the field is moved from an X peak to the adjacent Y peak[5] and by studies of the orientation dependence of the transients in single crystals.[6]

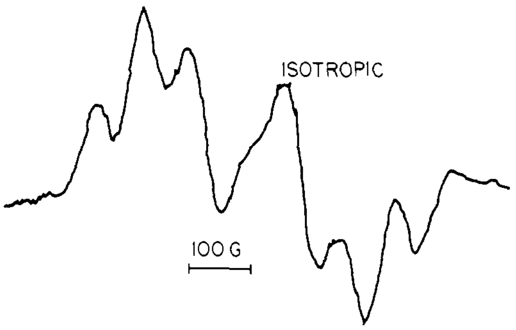

Figure 5. CW EPR spectrum **1** produced by unpolarized tightly convergent beam.

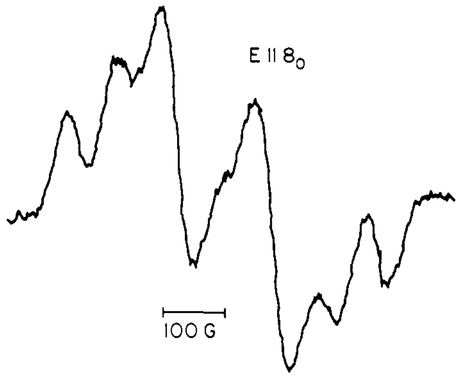

Figure 6. CW EPR spectrum of **1** produced by light with $\vec{E} \parallel B$.

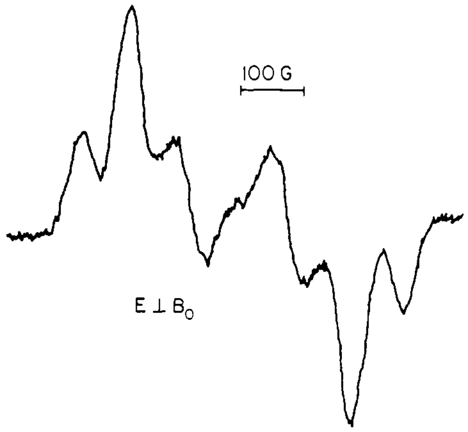

Figure 7. CW EPR spectrum of **1** produced by light with $E \perp B$.

Chart II

polarization	transition moment	$f(\theta,\xi)$
$\vec{E} \parallel \vec{B}$	Z	$\cos^2\theta\ \sin\theta$
$E \perp B$	Z	$\frac{1}{2}\sin^3\theta$
$\vec{E} \parallel B$	Y	$\sin^3\theta\ \sin^2\xi$
$\vec{E} \perp B$	Y	$\frac{1}{2}(\cos^2\theta\ \sin^2\xi + \cos^2\xi)\sin\theta$
$E \parallel B$	X	$\sin^3\theta\ \cos^2\xi$
$E \perp B$	X	$\frac{1}{2}(\cos^2\theta\ \cos^2\xi + \sin^2\xi)\sin\theta$
unpolarized	~	$\sin\theta$

Figure 5–7 show the CW spectra for the isotropic case (unpolarized light, tightly convergent beam) and the two polarizations, $\vec{E} \parallel \vec{B}_0$ and $\vec{E} \perp \vec{B}_0$, where $\vec{E}$ and $\vec{B}_0$ represent the electric vector of the exciting light and the static magnetic field. The differences are striking. The assignment is almost obvious from the qualitative features of the spectra: when $\vec{E} \parallel \vec{B}_0$ the X peak dominates, and when $\vec{E} \perp \vec{B}_0$ the Y peak dominates. One would guess that the transition moment of the precursor is parallel to the x principal axis of the biradical. We confirm the guess by simulations of the

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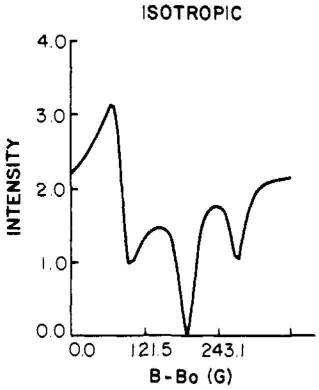

Figure 8. Simulated isotropic spectrum with $1/T_2$ = 15 G.

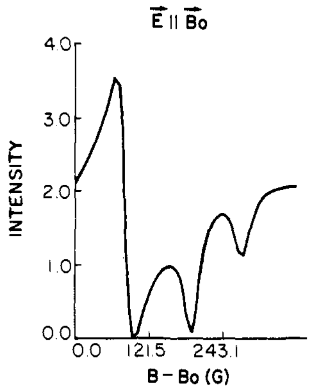

Figure 9. Simulated spectrum for $\vec{E} \parallel \vec{B}$ transient moment along X. Partial depolarization as described in text.

spectra. The simulations are carried out under the simplifying assumptions that the line shape for fixed orientation may be approximated as Lorentzian with line width parameter $1/T_2$ and all orientations having the same T_2. A first-order perturbation calculation is adequate since the external magnetic field is an order of magnitude larger than the internal dipolar field. Parameters in gauss used in the simulations are D = 274.3, E = 36.4, $1/T_2$ = 15.

The spectral shape function $\mathrm{d}\chi''/\mathrm{d}B$ is given by[7]

$$\frac{\mathrm{d}\chi''}{\mathrm{d}\Delta} = \int_0^{\pi} \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\zeta \left[\frac{T_2F_1}{\{T_2F_1{}^2 + 1/T_2\}^2} + \frac{T_2F_2}{\{T_2F_2{}^2 + 1/T_2\}^2} \right] f(\theta,\zeta)$$

where $\Delta = B - B_0$

$$F_1 = \Delta - (D/2)(1 - 3\cos^2\theta) + 3E/2 \sin^2\theta\,(1 - 2\sin^2\zeta)$$

$$F_2 = \Delta + (D/2)(1 - 3\cos^2\theta) - 3E/2 \sin^2\theta\,(1 - 2\sin^2\zeta)$$

θ and ζ are Eulerian angles describing the molecular orientation in the laboratory frame. θ is the angle between $\vec{B}$ and the molecular z axis; ζ is chosen so that when $\theta = \pi/2$, the molecular x axis is parallel to B at $\zeta = 0$. $f(\theta,\zeta)$ is the distribution function appropriate for the orientation of the electric vector relative to B_0 and to the direction of the transition moment in the molecule. We list $f(\theta,\zeta)$ for the cases of interest as indicated in Chart II.

We could not achieve a satisfactory fit to the observed spectra under the assumptions of perfect polarization of the light and photolysis of only a negligible fraction of the precursor. The multiple reflections and scattering in the Dewar flask and the imperfection of the glassy medium contribute to depolarization. We achieved good agreement with the experimental spectra by adding to the ones calculated for perfect polarization equal contribution of isotropic distributions. (This procedure is equivalent to having 75% polarization). Simulated spectra are shown in Figures 8–10.

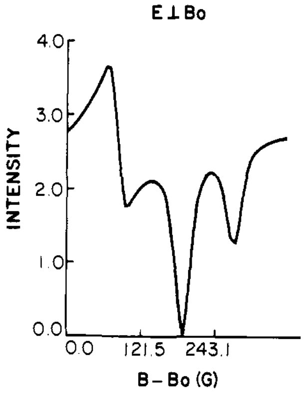

Figure 10. Simulated spectrum for $\vec{E} \perp \vec{B}$ transition moment along X. Partial depolarization as described in text.

Our experiments have established that the biradical appears, following the photolytic pulse, in times short compared to the resolving time (~150 ns) of our transient magnetic resonance apparatus, that the biradical has $D > 0$ and is born predominantly in the T_z substate, and that the transition moment at 337 nm in the diazene precursor is approximately parallel to the magnetic principal axis of the biradical which corresponds to the innermost pair of peaks (labeled X) in the EPR spectrum.

We turn now to more speculative matters. How are the principal axes of the biradical oriented in the molecular frame? Unambiguous assignment could be made by studies of molecules with known alignments in single crystals of known structure. In the absence of such information we do what we can with structural considerations. The positive sign of D and the fact that the EPR spectrum of **1** is similar to that of trimethylenemethane lead to assignment of Z to the direction perpendicular to the plane. Since we have based our analysis on assignment of axes for which $E > 0$, and since E is proportional to $\langle y^2 - x^2 \rangle$, we ask which direction in the plane of the molecule fulfill this condition. Stereochemical and electronic considerations suggest the assignment shown in structure **2**.[8]

Studies of the fluorescence accompanying photolysis of the diazene by picosecond laser pulses[9-11] and analysis of reaction kinetics of the diyl[12] point to the passage of the system through a singlet state of the biradical following expulsion of the nitrogen. If the process in our experiment is

$$\text{diazene} \xrightarrow{337\ \text{nm}} \text{diazene*} \rightarrow \mathrm{N_2} + \text{singlet diyl} \rightarrow \mathrm{N_2} + \text{triplet diyl}$$

we conjecture that the singlet diyl has the same symmetry as the T_z state to which it crosses. The T_z state has the symmetry of an axial vector in the z direction: it is symmetric with respect to reflection in the molecule xy plane, antisymmetric with respect to reflection in the yz plane and with respect to a twofold rotation about the y axis. The dipole transition moment operator in the x direction has the same symmetry properties. We suppose then that the symmetry of the singlet state is that of a polar vector in the x direction. Calculations on trimethylenemethane[13] classify the excited singlet state in D_{3h} symmetry as doubly degenerate E. The degeneracy is lifted in the lower symmetry of the diyl **2**, one of the components having the x polar vector transformation properties.[14]

Our magnetophotoselection experiments establish the orientation of the transition moment in the precursor diazene relative to the

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J. Am. Chem. Soc. 1984, 106, 4423–4427

magnetic axes of the product diyl. It is possible that the symmetry of the photoexcited diazene is conferred upon the singlet diyl. The dinitrogen is certainly produced in its ground electronic state ${}^1\Sigma_g{}^+$. (The first electronic excitation of N_2 to ${}^3\Sigma_u{}^+$ is at 50 200 cm^{-1}.) Approximate conservation of symmetry suggests that the polar x symmetry is conferred on the diyl fragment of the photodissociation.

Acknowledgment. Support by the National Science Foundation under CHE-812006 and CHE-8011399 is gratefully acknowledged.

Registry No. 1, 32553-01-8; **2**, 31689-32-4.

Chemoreception by an Excitable Liquid Membrane: Characteristic Effects of Alcohols on the Frequency of Electrical Oscillation

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Contribution from the College of General Education, University of Tokushima, Minamijosanjima-cho, Tokushima 770, Japan. *Received October 31, 1983*

Abstract: Studies were made on oscillations across a liquid membrane consisting of an oil layer, nitrobenzene containing picric acid, between two aqueous layers: that on the left containing 5 mM CTAB plus an alcohol at various concentrations and that on the right containing 0.1 M sucrose. This system showed sustained rhythmic oscillations of electrical potential of 200–400 mV with an interval on the order of 1 min. The frequency of oscillations increased with increase in the concentration of the alcohol. The critical concentration of alcohols needed to induce oscillations decreased with an increase in their hydrophobicity. The oscillations can be explained by a mechanism of repetitive formation and abrupt destruction of a monolayer structure of CTA$^+$ on the interface between the organic and aqueous phases. The response to alcohols in the liquid membrane apparently resembled that of biological cheomoreceptive membranes. The possibility was suggested of developing a new type of chemical sensor with the ability to distinguish various chemical substances from the patterns of electrical oscillation that they induced.

One of the most interesting phenomena in biological systems is excitability. There is much literature on electrical phenomena accompanying electrical excitation in biological membranes, but despite extensive studies on biooscillations, the physicochemical mechanisms of these phenomena are not yet clear. For an understanding of the mechanism of biological excitation and/or oscillation, various types of artificial membranes with excitability have been investigated.[1-6] Most of the artificial membranes examined were excitable under an external force, such as pressure,[1,2] voltage,[3,5] or electrical current.[3,4,6] In excitable biomembranes, it is well established that the difference in the compositions of electrolytes, especially potassium and sodium ions, across the membranes is important. Investigations on "self-excitable" artificial membranes are thus important in understanding the mechanism of excitation and/or oscillation in biological systems. However, there are very few report on this phenomenon in artificial membranes. Kobatake[4] found that porous membranes doped with dioleylphosphate, DOPH-Millipore membranes, showed spontaneous firing of an electrical potential when placed between solutions of different KCl concentrations. Pant and Rosenberg[7] observed that a lipid bilayer membrane separating bathing solution compartments of potassium ferricyanide and potassium iodide could be set into sustained electrical oscillations when the pH's of the two compartments were adjusted to 5 and 10, respectively. von Klitzing et al.[8] reported that voltage spikes were generated in a lipid bilayer membrane (black membrane) between aqueous solutions of different concentrations with KCl or KH_2PO_4, though they observed no dependence of these spikes on the electrolyte concentration.

Recently, we[9] found that electrochemical oscillations occur spontaneously even in a simple two-phase system consisting of an organic solution of picric acid in nitropropane and an aqueous solution of cetyltrimethylammonium bromide (CTAB). We also studied[10] an artificial liquid membrane consisting of an oil layer, nitrobenzene containing picric acid, imposed between two aqueous phases, one containing 5 mM CTAB and 5% ethanol. We found that this system showed rhythmic and sustained oscillations of electrical potential within the range of 150–300 mV with an interval of 2–3 min. No oscillations were observed in the absence of ethanol. As an extension of these studies, we investigated the effect of alcohols on the oscillations in the liquid membrane.

The present paper reports the results of these experiments, indicating that the frequency of the oscillations depends on the concentration of alcohols, and that the threshold concentration needed to induce electrical oscillations decreases with an increase in the "hydrophobicity" of the alcohols.

Experimental Section

Experiments were performed in an apparatus with a U-shaped glass tube (12-mm inner diameter). The apparatus is shown schematically in Figure 1. A solution (4 mL) of 1.5 mM picric acid in nitrobenzene was placed in the base of the U cell. Aqueous solutions (10 mL each) were introduced simultaneously into the arms of the U cell above the organic phase without stirring. All measurements were carried out at 25 °C. The

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