Mechanism of Thermolysis of Endoperoxides of Aromatic Compounds. Activation Parameters, Magnetic Field, and Magnetic Isotope Effects†

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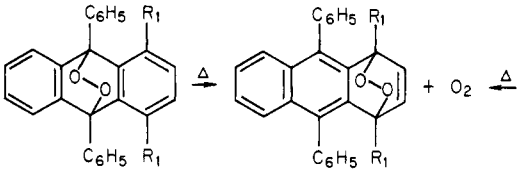
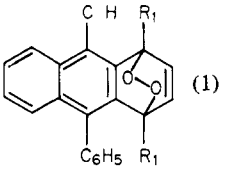
Abstract: A mechanistic investigation has been made of the thermolysis of several endoperoxides of anthracenes and naphthalenes which produce molecular oxygen and the parent aromatic species quantitatively. Qualitative thermochemical measurements in the solid state indicate that in all the cases studied, the reactions were endothermic. This situation appears to be valid in solution also. Clean first-order kinetics were observed for these thermolyses. Activation parameters were derived from the temperature dependence of the first-order rate constants. The primary yields of singlet molecular oxygen ($^1O_2$) from the several endoperoxides were determined, and a correlation was discovered between the A factors ($\Delta S^\ddagger$ values) for thermolysis and the yield of $^1O_2$. It was found that high A factors (positive $\Delta S^\ddagger$ values) correlated with relatively low yields of $^1O_2$, and that low A factors (slightly negative or near zero $\Delta S^\ddagger$ values) correlated with nearly quantitative yields of $^1O_2$. These two results are interpreted in terms of a diradical mechanism which leads to low yield of $^1O_2$ and a concerted mechanism which leads to quantitative yields of $^1O_2$, respectively. This interpretation is consistent with the observation of a magnetic field effect on the yield of $^1O_2$ from endoperoxides whose thermolyses proceed with positive $\Delta S^\ddagger$ values and the absence of a magnetic field effect on the yield of ^1O_i endoperoxides whose thermolyses proceed with near zero $\Delta S^\ddagger$ values. Further support for the occurrence of a diradical mechanism is available from the demonstration of a special ^{17}O isotope effect on the thermolysis of an endoperoxide which is postulated to undergo thermolysis principally via a diradical intermediate. The thermolysis of endoperoxides which decompose mainly by a diradical mechanism yields triplet molecular oxygen that is selectively enriched in ^{17}O.

The thermolyses of many endoperoxides of aromatic compounds (e.g., anthracene endoperoxides) are known to generate molecular oxygen and the parent aromatic species (eq 1).[1] The reactions



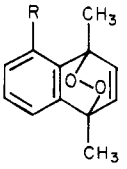
1, $R_1 = H$
2, $R_1 = CH_3$

5, $R_1 = H$
6, $R_1 = CH_3$
7, $R_1 = OCH_3$

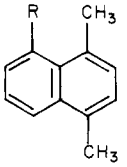


(1)

3, $R_1 = CH_3$
4, $R_1 = OCH_3$



8, R = H
9, $R = CH_3$



10, R = H
11, $R = CH_3$

listed in eq 1 are characterized by a charmingly simple structural reorganization; they proceed in quantitative yields at temperatures near or below 100 °C and possess the fascinating feature of chemiluminescence; i.e., singlet molecular oxygen, an electronically excited species, is produced as a primary product.[2] Although the synthetic utility of employing endoperoxides has been demonstrated,[2] at the onset of this study we were unaware of any detailed mechanistic studies which probed the details of the rate-determining step in endoperoxide thermolyses or of any thermochemical measurements[3] pertinent to the endoperoxide decompositions or any systematic measurements of the primary yield of singlet molecular oxygen ($^1O_2$) produced in thermolyses of endoperoxides of different structures. We report here (a) an investigation of the kinetics of thermolysis of several endoperoxides, (b) evaluation of the activation parameters for these thermolyses, (c) measurement of primary yield of $^1O_2$ which is produced upon thermolysis, (d) observation of magnetic isotope and magnetic field effects on the course of thermolyses, and (e) demonstration that the thermolyses may be employed as a novel method for selective separation of ^{17}O from ^{16}O and ^{18}O.

Results

Product Analysis. Each of the endoperoxides (EP) shown in eq 1 was subjected to thermolysis in several solvents. The observed behavior was qualitatively similar in all cases studied: the parent aromatic (PA) compound was produced in good (≳95%) yield and molecular oxygen was the only detectable gas produced (by mass spectrometry). When tetracyclone and 9,10-dimethylanthracene were used as singlet oxygen acceptors,[4] the corresponding singlet oxygen oxidation products, 1,2,3,4-tetraphenyl-2-butene-1,4-dione (IR, TLC analysis) and 9,10-dimethylanthracene 9,10-endoperoxide (TLC and NMR analysis), were the only detectable products. Although 2,5-dimethylfuran was also used as a singlet oxygen acceptor, there was no attempt

† Dedicated to George S. Hammond on the occasion of his 60th birthday.
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‡ Columbia University.
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(1) Moureu, C.; Dufraisse, C.; Dean, P. M. *C. R. Hebd. Seances Acad. Sci.* **1926**, *182*. Rigaudy, J.; Guillaume, J.; Maurette, D. *Bull. Soc. Chim. Fr.* **1971**, 144.
(2) Wasserman, H. H.; Scheffer, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 3073. Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. *Ibid.* **1972**, 94, 4991.
(3) Estimates of standard enthalpies of formation of endoperoxides based on group additivities are in considerable disagreement with the values measured in this work for the solid-state thermolysis. These estimates, however, lead to a discrepancy between predicted and observed activation energies for endoperoxide thermolysis: Stevens, B.; Small, R. D. *J. Phys. Chem.* **1977**, *81*, 1605.
(4) Stevens, B.; Perez, S. R. *Mol. Photochem.* **1974**, *6*, 1. Koch, E.; *Tetrahedron* **1968**, *24*, 6295. Foote, C. S.; Wexler, S. J. *J. Am. Chem. Soc.* **1964**, *86*, 3879.

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Table I. Activation Parameters, Singlet Oxygen Yields, and Reaction Enthalpies for Thermolyses of Endoperoxides

compd	temp range, °C	rate constant range, s^{-1}	$\Delta E^{\ddagger}$, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, esu	% $^1O_2$ yield	ΔH, kcal/mol	
								f	g
1	60.2[a]	$(4.50 \pm 0.06) \times 10^{-7}$	33.2 ± 0.2	15.4 ± 0.1	32.5 ± 0.2	9.6 ± 0.5	32 ± 1	6 ± 1	10 ± 2
	92.2	$(3.73 \pm 0.09) \times 10^{-5}$							
	66.2[b]	$(1.70 \pm 0.01) \times 10^{-6}$	32.1 ± 0.2	14.9 ± 0.1	31.4 ± 0.2	7.3 ± 0.5	35 ± 3		
	91	$(4.40 \pm 0.06) \times 10^{-5}$							
	65.1[c]	$(7.0 \pm 0.6) \times 10^{-7}$	33.0 ± 0.9	15.2 ± 0.6	32.3 ± 0.9	9 ± 3	...		
	86	$(1.24 \pm 0.08) \times 10^{-5}$							
	65.1[d]	$(7.4 \pm 0.7) \times 10^{-7}$	32.9 ± 0.9	15.2 ± 0.6	32.2 ± 0.9	9 ± 3	...		
	86	$(1.38 \pm 0.09) \times 10^{-5}$							
	65.1[e]	$(1.04 \pm 0.06) \times 10^{-6}$	31.6 ± 0.6	14.5 ± 0.4	30.9 ± 0.6	5 ± 2	...		
	86	$(1.78 \pm 0.09) \times 10^{-5}$							
2	60.2[a]	$(4.4 \pm 0.2) \times 10^{-7}$	32.5 ± 0.3	14.9 ± 0.2	31.8 ± 0.3	7.4 ± 0.8	52 ± 4	4 ± 1	9 ± 2
	92.2	$(3.24 \pm 0.07) \times 10^{-5}$							
	66.2[b]	$(1.74 \pm 0.01) \times 10^{-6}$	30.3 ± 0.4	13.7 ± 0.3	29.6 ± 0.4	2 ± 1	73 ± 2		
	91	$(3.53 \pm 0.07) \times 10^{-5}$							
3	73.2[a]	$(4.3 \pm 0.2) \times 10^{-7}$	30.5 ± 0.3	13.0 ± 0.2	29.8 ± 0.3	−1.8 ± 0.8	92 ± 1	9 ± 1	7 ± 1
	97	$(7.3 \pm 0.1) \times 10^{-6}$							
4	15.1[a]	$(2.09 \pm 0.08) \times 10^{-6}$	24.8 ± 0.3	13.0 ± 0.2	24.2 ± 0.2	−0.3 ± 0.7	95 ± 5	2 ± 1	1 ± 1
	35	$(3.5 \pm 0.1) \times 10^{-5}$							
8	12[a]	$(5.3 \pm 0.1) \times 10^{-6}$	24.8 ± 0.2	13.7 ± 0.2	24.2 ± 0.2	2 ± 1	76 ± 1		
	35	$(1.28 \pm 0.01) \times 10^{-4}$							
9	24.8[a]	$(2.10 \pm 0.04) \times 10^{-6}$	26.6 ± 0.2	13.8 ± 0.1	26.0 ± 0.2	2.6 ± 0.5	69 ± 1		
	57.2	$(7.57 \pm 0.08) \times 10^{-5}$							

[a] Solvent: 1,4-dioxane. [b] Solvent: chlorobenzene. [c] Solvent: benzonitrile. [d] Solvent: dodecane. [e] Solvent: toluene. [f] Measurements in solid state. [g] Calculated from activation parameters and assumption of 0 activation energy for reaction of singlet oxygen. See text for discussion.

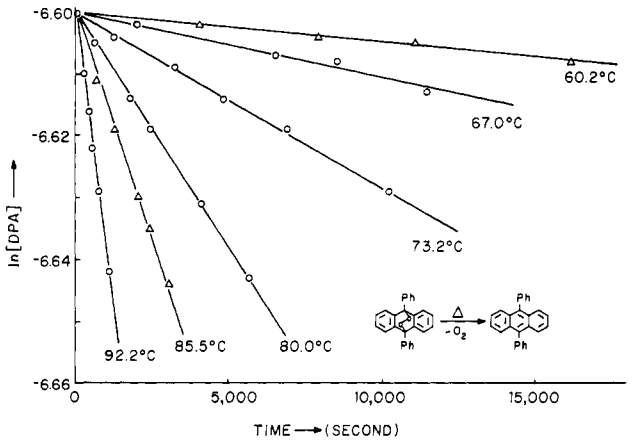


Figure 1. Kinetic data for the disappearance of 9,10-diphenylanthracene endoperoxide in the thermolysis of 9,10-diphenylanthracene endoperoxide in *p*-dioxane.

to identify the reaction products in this case.

Kinetics and Activation Parameters. The appearance of PA measured by UV absorptivity was monitored as a function of time at various temperatures. In each case excellent first-order kinetics were observed (Figure 1). The Arrhenius parameters were computed in the usual fashion from a plot of the log of the first-order rate constants vs. the reciprocal of the absolute temperature. Typical data of the thermolysis in 1,4-dioxane are given in Figure 2. The activation parameters ($\Delta E^{\ddagger}$, A) as well as the associated activation enthalpies ($\Delta H^{\ddagger}$) and activation entropies ($\Delta S^{\ddagger}$) derived from Eyring plots are summarized in Table I.

Qualitative Measurement of Reaction Enthalpies for Solid-State Thermolyses. The reaction heats for thermolyses of solid anthracene endoperoxides were measured employing the method of differential scanning calorimetry.[5a] With the assumption that molecular oxygen is an ideal gas, the reaction enthalpies were computed (Table I). The measured enthalpies are expected to be qualitatively similar to the solution thermolyses because the reactants and products are nonpolar organic compounds and should have similar energies of solvation. The measured reaction enthalpies for solid-state thermolysis are summarized in Table I. It was found that the thermolyses of all the anthracene endoperoxides studied are *endothermic* reactions, (+1 to +9 kcal/mol).

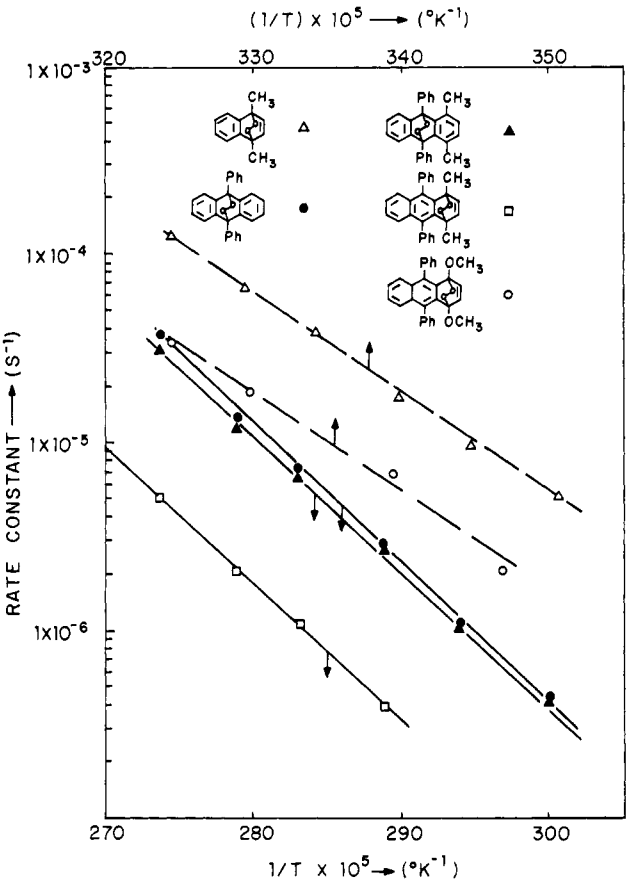
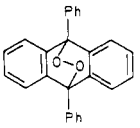
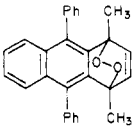
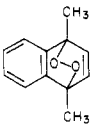
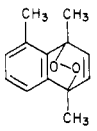


Figure 2. The plot of rate constants of thermolyses of aromatic endoperoxides as a function temperature in *p*-dioxane.

Measurement of the Singlet Oxygen Yield. Two singlet molecular oxygen acceptors, tetracyclone (TC) and 9,10-dimethyl-

(5) (a) Pitzer, K. S.; Brewer, L. "Thermodynamics"; McGraw-Hill: New York, 1961. Hoyer, H. W.; Birdi, K. S. *Biopolymers* **1968** *6*, 1509. Hoyer, H. W.; Chow, M. *J. Colloid Interface Sci.*, in press. (b) Olmsted, J. *J. Am. Chem. Soc.* **1980**, *102*, 66.

Table II. Correlation of Activation Entropies, Singlet Oxygen Yield, and Magnetic Field Effect in Endoperoxide Thermolyses

endoperoxide	$\Delta S^{\ddagger}$, eu	singlet oxygen yield, % 0.5 G	4500 G	9500 G	11 500 G	13 000 G	15 500 G	17 000 G
 **1**	+10	32 ± 1		30 ± 3	27 ± 2	23 ± 2		
 **3**	−2	92 ± 1		93 ± 2		91 ± 4		
 **8**	+2	76 ± 1	76 ± 0.5	73 ± 1			71 ± 0.5	70.5 ± 0.5
 **9**	+3	69 ± 1				66.0 ± 0.6	67.0 ± 0.5	

anthracene (DMA), were employed to measure the yield of singlet molecular oxygen generated from EP. The choice of acceptor was determined by the required experimental conditions; i.e., TC and DMA were employed at 90 and 40 °C, respectively. The yield of singlet molecular oxygen was determined by the ratio of disappearance of acceptor to the appearance of PA. It was demonstrated that DMA quenches singlet molecular oxygen mainly via a chemical process (≥90%). It has been reported that at room-temerpature physical quenching is an important deactivation pathway for TC as a singlet molecular oxygen quencher.[6] This was confirmed in our experiments. When **4** was thermolyzed in dioxane solution at room temperature with TC as a $^1O_2$ trap, the yield of singlet molecular oxygen was determined as ca. 50%. However, when **3** and **4** were thermolyzed at 90 °C with TC as a $^1O_2$ trap, the yields of singlet molecular oxygen were 92% and 95%, respectively. These results suggest that physical quenching by TC becomes less important at higher temperatures. The singlet oxygen yields summarized in Tables I–III were the average of eight or more measurements. The error given refers to standard deviation.

Magnetic Field Dependence of the Singlet Oxygen Yield. When the EP's **1**, **3**, **8**, and **9** were thermolyzed in an external magnetic field, the yields of singlet oxygen changed in a mannger that depended on the EP's studied. The data in Table II show that the thermolysis of **1** had the largest magnetic field dependence for fields up to ~15 000 G. The relative change for **1** is 30%, from 32% yield of $^1O_2$ to 23% yield of $^1O_2$. On the other hand, the thermolysis of naphthalene endoperoxides showed a relatively small magnetic field effect ca. 5% for fields up to 15 000 G. The rate constants of the thermolyses of the EP's were found to be magnetic field independent. For example, **8** had the same rate constants measured in a magnetic field of an NMR spectrometer and in the earth's magnetic field. UV measurement was employed for the latter case. Also, for a given time period, the thermolyses of **1** proceed to the same conversion at 10 000 G and in the earth's magnetic field.

(6) Evans, D. F.; Tucker, J. N. *J. Chem. Soc., Faraday Trans. 2*, **1976**, *72*, 1661.
(7) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972.
(8) Kaptein, R.; VanLeeuwen, P. W. N. M.; Huis, R. *Chem. Phys. Lett.* **1976**, *41*, 264.

Table III. Yield of $^1O_2$ Formation and Isotopic Effect in the Thermolysis of **1**

% yield of $^1O_2$[a] ^{16}O[b]	$^{17,18}O$[c]	^{18}O[d]	magnetic field	solvent
37 ± 1	34 ± 1	37 ± 1	0.5 G	$CHCl_3$
32 ± 2	31 ± 1	31 ± 1	10 KG	$CHCl_3$
32 ± 1	28 ± 1	32 ± 2	0.5 G	dioxane
27 ± 2	23 ± 1	28 ± 2	12 KG	dioxane
28.3 ± 0.3	27.2 ± 0.2	28.4 ± 0.2	0.5 G	benzene
27.8 ± 0.8	27.8 ± 0.7	28.1 ± 0.8	10 KG	benzene

[a] The yield of $^1O_2$ is defined as the ratio of disappearance of tetracyclone to the appearance of **5**. The yield is derived directly from the mixed isotopic oxygen containing **1** employed; i.e., no adjustment in yield is made for the differing percents of ^{16}O, ^{17}O, and ^{18}O in the starting material **1**. The error given is the standard deviation derived from a minimum of eight independent samples measured once. [b] The initial isotopic composition is 99.8% ^{16}O, i.e., natural abundance oxygen. [c] The initial isotopic composition is 60% ^{18}O and 37% ^{17}O (and 3% ^{16}O). [d] The initial isotopic composition is 92% ^{18}O and 4% ^{17}O (and 4% ^{16}O).

Isotope Effects on the Yield of Singlet Oxygen. Significant magnetic field effects were observed on the singlet oxygen yield of the thermolysis of ^{17}O enriched **1** in $CHCl_3$ and 1,4-dioxane (Table III). However, there were no magnetic field effects observed in benzene.[14b] Significantly, the same yield of singlet oxygen was generated from the thermolyses of **1** (natural abundance) and **1**-^{18}O-98%. There were no isotope effects on the yield of singlet molecular oxygen generated from **9**-^{17}O-37% observed in 1,4-dioxane and chloroform.

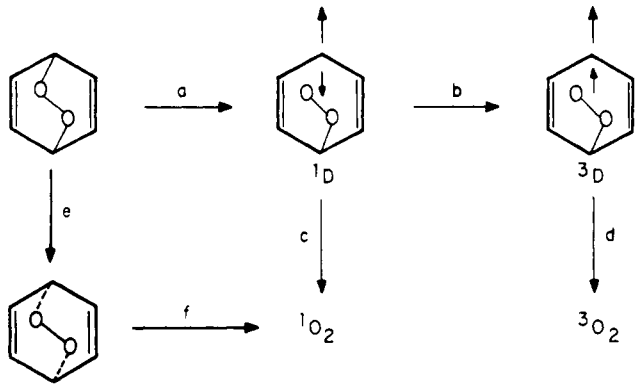
^{17}O Isotopic Enrichment in the Thermolysis of Endoperoxides. Residual molecular oxygen recovered from photooxidation of **5**, **11**, and **7** had the same ^{17}O composition as the molecular oxygen employed to prepare **1**-^{17}O-37%. Furthermore, the molecular oxygen generated by the thermolysis of **1**-^{17}O-37% and **9**-^{17}O-37% in the absence of singlet molecular oxygen acceptor had the same ^{17}O composition as the molecular oxygen employed to make the endoperoxides. However, in the presence of tetracyclone an increase in ^{17}O in the nontrapped molecular oxygen was observed from the thermolyses of **1**-^{17}O-37% in $CHCl_3$ and 1,4-dioxane (but not in benzene). If the thermolysis of **1**-^{17}O-37% was run in a magnetic field of about 10 000 G, enrichment of ^{17}O in the

Table IV. ^{17}O Composition of Nontrappable O_2 Generated from the Thermolysis of Endoperoxides

endo-peroxide	^{17}O composition	magnetic field	solvent
9[a]	36.9 ± 0.3	0.5 G	$CHCl_3$
	37.0 ± 0.3	15 KG	$CHCl_3$
1[b]	38.0 ± 0.5	0.5 G	$CHCl_3$
	36.8 ± 0.2	10 KG	$CHCl_3$
	37.6 ± 0.1	0.5 G	dioxane
	37.6 ± 0.2	12 KG	dioxane
	36.9 ± 0.1	0.5 G	benzene
	36.9 ± 0.4	10 KG	benzene
9, 1[c]	36.9 ± 0.1		$CHCl_3$/ dioxane/ benzene

[a] In the presence of DMA. [b] In the presence of tetracyclone. [c] In the absence of any $^1O_2$ acceptor.

Scheme I



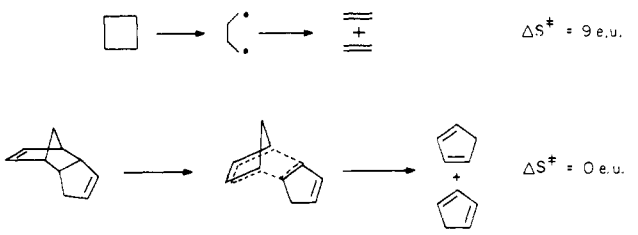
nontrapped oxygen was observed in 1,4-dioxane, but not in $CHCl_3$ and benzene (Table IV). No enrichment of ^{17}O in the nontrapped O_2 was observed in the thermolysis of 9-^{17}O-37% in chloroform in the presence of DMA.

Discussion

Mechanism of Endoperoxide Thermolyses. Correlation of Diradical and Concerted Pathways with Activation Parameters. Some of the key parameters in an analysis of the mechanism of endoperoxide thermolyses are (1) the activation enthalpies and entropies, (2) the reaction enthalpies, (3) the singlet oxygen yields, (4) the magnetic field effects on the singlet oxygen yield, and (5) the oxygen isotope effects on the singlet oxygen yields. A working mechanism to serve as a basis for discussion is given in Scheme I, where only the key group of atoms involved in the thermolyses is shown. We postulate two basic and potentially competing pathways: (1) a diradical sequence produces a primary intermediate singlet diradical capable of fragmenting to produce $^1O_2$ or undergoing intersystem crossing to a triplet diradical capable of fragmenting to produce $^3O_2$; (2) a concerted pathway which produces $^1O_2$ directly. If pathway 1 is followed, then A (or $\Delta S^{\ddagger}$) is expected to be of a magnitude typical for formation of a diradical, whereas if pathway 2 is followed, then A (or $\Delta S^{\ddagger}$) is expected to be of a magnitude typical of concerted pericyclic reactions. Inspection of the literature[9] shows that a value of $A \approx 10^{15.6}$ s^{-1} ($\Delta S^{\ddagger} \approx +8$ to $+10$ eu) is typical of molecule → diradical reactions (e.g., the thermolysis of cyclobutane, Scheme II), whereas a value of $A \approx 10^{13}$ s^{-1} ($\Delta S^{\ddagger} \approx 0$ eu) is typical of concerted reactions (e.g., the thermolysis of endodicyclopentadiene, Scheme II).

On the basis of the postulate that an endoperoxide decomposes predominantly by either the diradical pathway 1 or by the concerted pathway 2, the thermolyses of 9,10-anthracene endoperoxide

Scheme II



are readily classified as diradical reactions, whereas the thermolyses of 1,4-anthracene endoperoxides are classified as concerted reactions; i.e., a correlation between $^1O_2$ yields and $\Delta S^{\ddagger}$ exists and this correlation allows mechanistic distinctions to be made.

Correlation of Activation Parameters and Singlet Oxygen Yields. Under the simplifying postulate that either pathway 1 or 2 is followed exclusively for any given endoperoxide, it is a natural consequence that anthracene 1,4-endoperoxides will produce $^1O_2$ quantitatively. This expectation is fully vindicated (Table I). It should be noted, parenthetically, that the decomposition of **3** and **4** are the most efficient chemiexcitation reactions of organic molecules yet discovered.[10] It is not possible to anticipate quantitatively the yield of $^1O_2$ from anthracene 9,10-endoperoxides because the extent of partitioning of ^1D between reaction to produce $^1O_2$ (path c, Shceme I) and intersystem crossing to form ^3D (path b, Scheme I) and the extent of concerted reaction cannot be predicted. However, the occurrence of path b to any significant extent opens the possibility that the yields of $^1O_2$ from molecules which react via a diradical pathway may be dependent on magnetic effects. We are unaware of any obvious means by which the yield of $^1O_2$ from molecules which react via a concerted pathway can be subject to significant magnetic effects.

Correlation of the Diradical Pathway with Magnetic Field Effects. The rate of singlet–triplet crossing (k_{ST}) from ^1D to ^3D is expected to depend to some extent on the strength of applied laboratory fields.[11] This dependence arises because for strong enough external fields k_{ST} for a diradical possessing degenerate (or nearly degenerate) singlet and triplet levels will be proportional to ΔgH where Δg is the difference in g factors at the two radical centers and H is the strength of the applied field.[12] The magnitude of Δg is expected to be substantial ($\sim$0.01) for a diradical possessing a peroxy and a carbon radical center. Typical values of Δg for two carbon-centered radicals are $\sim$0.001. As an order of magnitude approximation if $\Delta g \approx 10^{-2}$ and $H \approx 10\,000$ G, the value of ΔgH is $\sim 10^8$ s^{-1}. The rates of decay of diradicals are of this order, so that, from Scheme I, it is conceivable that the yield of $^1O_2$ from thermolysis of anthracene 9,10-endoperoxides may be magnetic field dependent. However, the yield of $^1O_2$ from anthracene 1,4-endoperoxides (concerted reaction) should not be magnetic field dependent, and the $^1O_2$ yield should remain constant as H increases. These qualitative expectations are in full agreement with the data in Table II.

Correlation of Diradical Pathway with an Anomalous Oxygen-17 Isotope Effect. The rather remarkable possibility of a magnetic isotope effect on the partitioning of ^1D is apparent from Scheme I. At zero external magnetic field, the probability (P_{ST}) of intersystem crossing from ^1D to ^3D may be estimated[11] from eq 2,

$$P_{ST} = P_{ST}^0 + (3/16)A^2t^2 \qquad (2)$$

where A^2 is the sum of the squares of the pertinent hyperfine couplings, t is the pertinent time interval, and P_{ST}^0 is the prob-

(9) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *NSRDS-NBS 21*.

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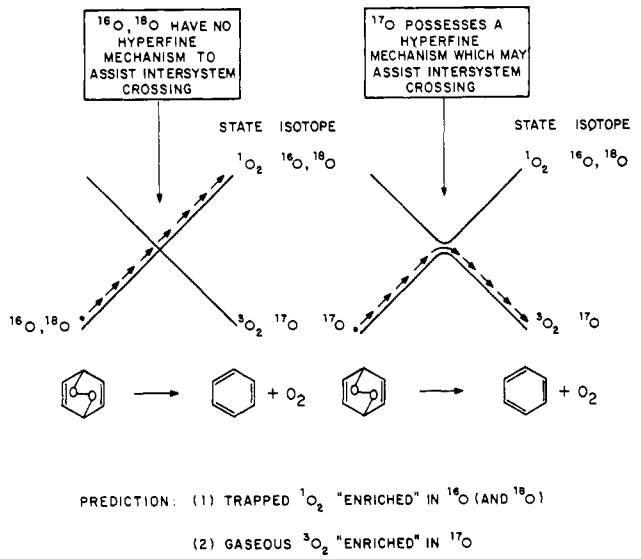
Scheme III



ability of intersystem crossing by mechanisms other than hyperfine interactions. From eq 2 it is clear the a ^1D species containing ^{17}O (a magnetic nucleus) will have a higher probability of undergoing $^1D \rightarrow {}^3D$ intersystem crossing than a ^1D species containing only ^{16}O and/or ^{18}O (nonmagnetic nuclei) simply because the occurrence of a magnetic nucleus *must* increase P_{ST} relative to its value in the absence of magnetic nuclei. Should this be the case, ^3D will be produced faster and $^3O_2$ will be produced in higher yield from endoperoxides possessing ^{17}O isotopes (Scheme III).

These theoretical considerations can be transformed into the following experimental expectations: If the diradical pathway is followed, the yield of $^1O_2$ will be *smaller* for endoperoxide molecules containing ^{17}O atoms than for endoperoxide molecules containing ^{16}O and/or ^{18}O atoms. A corollary is the experimental expectation that if $^1O_2$ produced by thermolysis is trapped selectively and quantitatively as the reaction occurs, the (untrapped) $^3O_2$ produced will be enriched in ^{17}O!

Both of these expectations were confirmed experimentally each by an independent type of measurement: (a) the ^{17}O and (^{16}O + ^{18}O) content of untrappable oxygen was analyzed by mass spectrometry and (b) the yield of trapped $^1O_2$ was evaluated by quantitative determination of the amount of reacted acceptor, when **1**-$^{16}O_2$, **1**-$^{18}O_2$, or **1**-$^{17}O_2$-37% were employed. From Table III it can be seen that the yield of $^1O_2$ formation is smaller for **1**-$^{17}O_2$-37% than for **1**-$^{16}O_2$ or **1**-$^{18}O_2$. The fact that both **1**-$^{16}O_2$ and **1**-$^{18}O_2$ produce the *same* yield of $^1O_2$ while **1**-$^{17}O_2$-37% produce less $^1O_2$ rules out a significant mass isotope effect as the basis for different yields. Furthermore (Table III), we observe that the results change quantitatively when reactions are run in a laboratory magnetic field, a result which confirms the conclusion that a magnetic spin isotope effect is operating.[14]

Since the amount of reacted trap is monitored in the yield measurements, they only provide an *indirect* test of the isotopic enrichment. A *direct* measurement involves determination of the isotopic composition of the untrappable molecular oxygen produced in the thermolysis of **1**-O_2. Table IV lists the isotopic composition of untrapped molecular oxygen produced from thermolysis of **1**-O_2 in $CHCl_3$ and in dioxane. The results demonstrate that the untrappable molecular oxygen is indeed enriched in ^{17}O relative to the control sample.

Correlation of the ^{17}O Isotope Effect on $^1O_2$ Yields and ^{17}O Enrichment. Application of eq 2 allows a qualitative correlation of the ^{17}O isotope effect on $^1O_2$ yields and on ^{17}O enrichment, if both effects operate by a hyperfine coupling mechanism. Under the assumptions that A^2 is dominated by ^{17}O hyperfine coupling, the magnitude of A^2 is calculated to be ~750 and ~370 G for ^1D-containing two ^{17}O atoms and for ^1D-containing one ^{17}O atom, respectively. For **1** in 1,4-dioxane the yield of $^1O_2$ is (32 ± 1)% for both ^{16}O and ^{18}O endoperoxides. Let the yield of $^1O_2$ from **1** containing two ^{17}O molecules and one ^{17}O molecule be (32 − x)% and (32 − $x/2$)%, respectively. Experimentally, the yield of $^1O_2$ from **1**-37% ^{17}O is (28 ± 1)% in 1,4-dioxane solvent. The $^1O_2$ yield for **1** containing two ^{17}O atoms and for **1** containing one ^{17}O atom is estimated to be (21 ± 1)% and (27 ± 1)%, respectively. Under the condition of quantitative trapping of $^1O_2$ produced from thermolysis of **1**, the ^{17}O composition of the untrapped molecular oxygen from **1**-^{17}O-37% is computed to be (38.7 ± 1)%, in good agreement with experiment (Table IV).

Relationships between the Thermolysis of Endoperoxides and the Reaction of Molecular Oxygen with Aromatic Compounds. An interesting question arises concerning the relationship of the [4 + 2] cycloaddition reaction of $^1O_2$ with aromatic compounds and the [4 + 2] retrocycloaddition reaction of aromatic endoperoxides. From information in the literature, $\Delta H^{\ddagger}$ is 0 ± 1 kcal/mol for the quenching of $^1O_2$ with a wide variety of substrates.[18] The differences in the quenching rate constants for ^1O_i are dominated by the $\Delta S^{\ddagger}$ term. The reactions of $^1O_2$ with dienes and aromatic compounds are generally considered to be concerted [4 + 2] cycloadditions (although the occurrence of perepoxide and/or related intermediates may be involved in certain cases). If the thermolysis of an aromatic endoperoxide to produce $^1O_2$ is the microscopic reverse of the reaction of $^1O_2$ with the corresponding aromatic compound, there is *essentially* no activation for the reverse reaction, and the value of ΔH for the reactions can be evaluated from knowledge that 22.5 kcal/mol of energy is required to produce $^1O_2$ from $^3O_2$ and the activation enthalpy for thermolysis of the endoperoxide

$$\Delta H_{AO_2}^{\ddagger} - 22.5 \text{ kcal/mol} = \Delta H$$

From our data (Table I), $\Delta H^{\ddagger}$ for the endoperoxide **1** is 32 ± 2 kcal/mol. Thus, if thermolysis of **1** proceeds by a concerted reaction that is the microscopic reverse of the addition of $^1O_2$ to **5**, the value of 10 ± 2 kcal/mol is computed for the reaction enthalpy. This value is within the error of the value[5b] of ΔH = 13 ± 5 kcal/mol for the photooxidation of **5**.

With the assumption that values of ΔH measured for solid-phase thermolysis are adequate for a discussion of the solution thermolyses, the competition between concerted one-step and diradical two-step mechanisms may be considered in the context of the microscopic relationship between the thermolysis and the addition of $^1O_2$ to anthracenes. Since the value of $\Delta H^{\ddagger}$ for the quenching of $^1O_2$ by a wide range of structures is 0 ± 1 kcal/mol, values of ΔH for the thermolysis may be calculated on the basis of the assumption of microscopic reversibility. In this regard, the thermochemical data for the thermolysis of **6** and **7** ± 5 to proceed by a concerted [4 + 2] retrocycloaddition) is fully consistent with the thermolysis as the microscopic reverse of the addition of $^1O_2$ to the pertinent anthracenes.

On the other hand, thermochemical data for the thermolysis of **1** and **2** are consistent with a diradical mechanism, although this need not be the exclusive pathway; i.e., the data are also consistent with a competition between concerted and diradical mechanisms. Furthermore, the basic assumption of microscopic reversibility demands that identical reactants and products are involved in the individual elementary chemical step under analysis. Since the thermolyses of **1** and **2** produce PA, singlet molecular oxygen, and triplet molecular oxygen, the products are different from the reactants for photooxidation of **5** and **6**, i.e., PA and singlet molecular oxygen only. Thus, the thermolysis of **1** and **2** and the *concerted* photooxidation of **5** and **6** are not related by microscopic reversibility.

The free energy difference between concerted and diradical pathways is of the order of several kilocalories per mole. Evidently, the diradical pathway requires a slightly higher enthalpy of activation than the concerted pathway but enjoys a more favorable

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activation entropy. Both cycloelimination pathways, furthermore, compete with a third process, the cleavage of the O–O bond. In the case of unsubstituted anthracene, the latter process dominates.[1]

Conclusion

The results of our studies allow a number of insights to the mechanism of the fragmentation of endoperoxides into molecular oxygen and an aromatic compound and to the mechanism of addition of molecular oxygen to aromatic compounds. There are two mechanisms by which the fragmentation occur: a diradical mechanism involving the initial homolytic cleavage of a single C–O bond followed by eventual loss of O_2 (in a singlet or triplet state) and a mechanism involving the concerted cleavage of both C–O bonds. The primary yield of singlet oxygen is relatively low in the diradical mechanism and is nearly quantitative in the concerted mechanism. It is remarkable that for 1,4-endoperoxides *nearly all of the activation energy for reaction is taken up to produce electronic excitation for the singlet oxygen produced.* Thus, in spite of the fact that the overall reaction—endoperoxide → $^1O_2$ + aromatic compound—is *strongly endothermic*, the efficiency of the chemiexcitation process is exceptionally high. It is important to note that these results lead to the conclusion that activation energy can indeed be channeled *efficiently* into electronic excitation energy, a possibility that has been the subject of some discussion in the literature.[17]

These conclusions suggest that there should be a temperature effect on the $^1O_2$ from **1**. Indeed, at low magnetic fields ($\lesssim$100 G), the yield of $^1O_2$ was found to *increase* as the temperature *decreased*: $^1O_2$ yield yields 32% at 93 °C and 41% at 77 °C.

Magnetic field and magnetic isotope effects provide a novel means to test for reactions involving diradicals. Although a discussion of the theoretical details of the origin of these effects are beyond the scope of this paper,[11,12] it is interesting to note that the exchange interaction between the odd electrons of the postulated diradical (Scheme I) is not sufficient to completely suppress hyperfine-induced intersystem crossing. It follows that if the exchange interaction can be reduced, even larger ^{17}O isotope effects may be observed. It also follows that an enhanced exchange may completely supress the ^{17}O isotope effect. The latter situation may explain the failure to observe ^{17}O enrichment when benzene is employed as solvent.[8]

Experimental Section

9,10-Diphenylanthracene (**5**) was purified by passage through neutral alumina with CH_2Cl_2 solvent, followed by crystallization from hexanes. 9,10-Dimethylanthracene and tetracyclone (Aldrich) were recrystallized from pentane (three times) and CCl_4 (two times), respectively. 1,4-Dimethylnaphthalene (**10**, Aldrich) was purified by passage through a neutral alumina column. The 1,4,8-trimethylnaphthalene (**11**) was synthesized following literature procedures.[18] 1,4-Dimethyl-9,10-diphenylanthracene (**6**) and endoperoxides **2**, **3**, and **4** were prepared following literature procedures.[16] 1,4-Dimethoxy-9,10-diphenyl-anthracene (**7**) was obtained as a generous gift from Dr. Bruce Monroe, E.I. du Pont de Nemours, Inc. Oxygen gas enriched in ^{17}O and ^{18}O obtained from Monsanto Research Corp. Chlorobenzene was vacuum distilled. 1,4-Dioxane was distilled over sodium hydroxide under a N_2 atmosphere. Chloroform was distilled under a N_2 atmosphere. Only fresh distilled 1,4-dioxane and chloroform were used. Benzonitrile, dodecane, and toluene were spectrograde and were used as provided. A Gilford Model 250 spectrometer was employed for absorption measurements (optical density accuracy = 0.002).

Preparations of 9,10-Diphenylanthracene Endoperoxide, 1,4-Dimethylnaphthalene Endoperoxide, and 1,4,8-Trimethylnaphthalene Endoperoxide.[20] As a general procedure, 20 mL of a CH_2Cl_2 solution containing ca. 1 g of the appropriate aromatic hydrocarbon and ca. 2 mg of methylene blue was photolyzed with a tungsten lamp under continuous O_2 purging at room temperature for 3 h. (For 1,4-dimethylnaphthalene, the temperature should be below 5 °C for 3 days.) The methylene blue was removed by filtration through a neutral alumina column. The endoperoxide (yields were typically ≥80%) was crystallized from a 10:1 hexane/methylene chloride mixture. Isotope enriched endoperoxides were prepared by a procedure analogous to that described above except that isotopically enriched molecular oxygen was employed, and the reaction was run in a closed system.

Product Study. When solutions of the aromatic endoperoxides employed in this study were thermolyzed, the parent aromatic compound was the only organic product detectable by NMR, IR, and TLC. The absolute yield of the parent compound was typically over 95% (UV absorption spectrometry). Exceptions were found for the 1,4-endoperoxides under certain conditions. **3** produced an unknown compound (~20%) when thermolyzed in chlorobenzene, and **4** regenerated only ca. 50% of the parent anthracene in benzene and chloroform (NMR spectroscopy).

The only detectable product of singlet molecular oxygenation of tetracyclone at 90 °C is 1,2,3,4-tetraphenyl-2-butene-1,4-dione. The dione was identified by a combination of IR, TLC, and mass spectrometry. Tetracyclone was shown to be stable in nitrogen-saturated, fresh-distilled 1,4-dioxane at 90 °C for 10 h. In air-saturated freshly distilled dioxane, about 5% of tetracyclone (initial concentration 2×10^{-3} M) is consumed at 90 °C for 10 h. Tetracyclone is stable in chlorobenzene, chloroform, and benzene at 90 °C.

Singlet molecular oxygenation of 9,10-dimethylanthracene produced 9,10-dimethylanthracene endoperoxide quantitatively for reaction temperatures below 50 °C.

Kinetic Studies of Aromatic Endoperoxide Thermolyses. The change of concentration of endoperoxides with time were monitored by following the appearance of the UV absorption of the corresponding aromatic compounds. Two wavelengths were used to monitor the absorption of the aromatic compounds. The solution in the UV cuvette cell was maintained at a desired temperature within ±0.2 °C. Typically, the initial concentrations of anthracene and naphthalene endoperoxides were 1×10^{-3} and 5×10^{-3} M, respectively.

Measurement of the Rate Constants for the Disappearance of Endoperoxides in the Presence of a Singlet Oxygen Acceptor. The concentrations of anthracene formed were derived from the optical density readings at 420 (**6**), 406 (**7**), and 405 nm (**5**) after corrections for tetracyclone absorption. The rate constants for the disappearance of endoperoxides were found to be independent of the presence of tetracyclone. For example, the rate constants of **1** at 85 °C in chlorobenzene are $(2.6 \pm 0.1) \times 10^{-5}$ and $(2.7 \pm 0.3) \times 10^{-5}$ s^{-1} in the absence and presence of tetracyclone, respectively.

The disappearance of **8** in $CDCl_3$ was monitored by NMR in the presence of 9,10-dimethylanthracene in a temperature-controlled probe. The rate constants were found to be independent of the presence of 9,10-dimethylanthracene. For instance, the rate constants for **8** in $CDCl_3$ at 45 °C were $(5.4 \pm 0.5) \times 10^{-4}$ and $(5.2 \pm 0.5) \times 10^{-4}$ M in the presence and absence of 9,10-dimethylanthracene, respectively.

Measurements of the Heats of Reaction for Decompositions of Anthracene Endoperoxides. The reaction enthalpies for decompositions of anthracene endoperoxides in the solid phase were measured employing a Du Pont 990 thermal analysis system equipped with a differential scanning calorimeter cell. Typically, 1–2 mg of endoperoxides was used. The sample container was opened to the atmosphere. The reference for the measurements was air, and the temperature program rate was set at 20 °C/min. The first endothermic transition peaks were found at 197, 191, 200, and 70 °C for **1**, **2**, **3**, and **4**, respectively. These transitions were not reversible and involved a color change from white to yellow which can be associated with the transitions from endoperoxides to parent anthracenes. For **2**, the transitions are overlapped with reversible melting transition of **6**. The decomposition enthalpies were derived after the proper correction of melting enthalpy.

Magnetic Field Effect on the Yield of Singlet Oxygen Generated by Thermolysis of 1,4-Dimethylnaphthalene 1,4-Endoperoxide (8) and 1,4,8-Trimethylnaphthalene 1,4-Endoperoxide (9). The magnetic field was provided by an Alfa Model 4600 constant electromagnet. $CDCl_3$o solutions of naphthalene endoperoxides and 9,10-dimethylanthracene (DMA) in sealed NMR tubes were thermolyzed at 40 ± 1 °C, overnight at various fields strengths. The thermolyzed solutions were analyzed by NMR Spectroscopy (Brucker WP-80) equipped with a built-in data processing. The initial concentrations of **8** and 9,10-dimethylanthracene were 5.15×10^{-2} and 6.26×10^{-2} M, respectively. The initial concentrations of **9** and DMA were 6.0×10^{-2} and 7.2×10^{-2} M, respectively. The conversions of endoperoxides and DMA were ca. 95% and 60%, respectively. The data listed in Table II present the average of four of more independent measurements, and the error given refers to the standard deviation.

Singlet Oxygen Yield of 9,10-Diphenylanthracene Endoperoxide (1) and 1,4-Dimethyl-9,10-diphenylanthracene 9,10-Endoperoxide (2) in

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Chlorobenzene. The initial concentrations of **1**, and **2**, and tetracyclone were 6.54×10^{-4}, 6.5×10^{-4}, and 2.08×10^{-3} M, respectively. The nitrogen-saturated solutions were thermolyzed at 87 °C for 18 h. The disappearance of tetracyclone and the appearances of **5** and **6** were monitored via absorption spectrometry at 510 and 520 nm. The average singlet oxygen yields from three independent runs are listed in Table I.

Magnetic Field Effect on the Yield of Singlet Oxygen Generated by Anthracene Endoperoxides (1, 2, 3, and 4). The magnetic field including 0.5 G was provided by an Alfa Model 4600 constant electromagnet. Typically, the initial concentrations of **1** and tetracyclone in 1,4-dioxane were 2×10^{-3} and 4×10^{-3} M, respectively. The solution was contained in a sealed glass tube with a 2-nm diameter. Sixteen of the sealed tubes were placed in a large tube, in which the temperature was controlled by circulating water. The position of the large tube was adjusted to have the sample tubes in the middle of the magnet. Eight of the sample tubes contained the solution of **1** and tetracyclone; the other eight samples which contained the solution of tetracyclone only were employed as control experiments. The control experiments were run to test the stability of tetracyclone and provide the initial optical density reading of tetracyclone at 405, 496, and 504 nm for the measurements of Δ(**5**) and Δ(tetracyclone). The typical conversions of **1** and tetracyclone were 45% and 8% at 90 °C for 5 h, respectively. Similar procedures were performed for thermolysis of **1** in benzene, chloroform, benzonitrile, dodecane, and toluene and for the measurements of singlet oxygen formed from **3** and **4** in dioxane. The initial concentrations of **3** and tetracyclone were 1.78×10^{-3} and 4.01×10^{-3} M, respectively. The initial concentration of **4** and tetracyclone were 8×10^{-4} M. The typical conversions of **3** and tetracyclone were 14% and 6% at 90 °C for 10 h, respectively. The typical conversion of **4** and tetracyclone were 50% and 5%, respectively. The data reported represent the average of eight (or sixteen) independent measurements in addition to eight (or sixteen) control experiments. The error refers to the standard deviation.

Calibration of Mass Spectrometer with CO_2 and O_2. The isotopic composition of molecular oxygen was analyzed with a JEOL-JMS-07 mass spectrometer equipped with a voltage to frequency converter and multichannel analyzer. The analyses were calibrated with natural abundance CO_2 and O_2. The measured ratio of CO_2 peaks 44, 45, and 46 is 100:1.12:0.427 which agrees well with the literature values[21] 100:1.19:0.408. The measured ratio of O_2 peaks 32, 33, and 34 is 100:0.06:0.36 which agrees well with the reported value[21] 100:0.072:0.408.

Measurements of the Isotope Composition of Oxygen Molecules Generated from Endoperoxides. The degassed solutions of **1** and **9** were thermolyzed 12 h at 90 and 40 °C, respectively. After thermolysis, the solution was frozen at 77 K and the product molecular oxygen was transferred directly by diffusion into the mass spectrometer in which the oxygen was analyzed. Typically, the initially concentrations of **1**, tetracyclone, **9**, and DMA were ca. 0.015 M. The conversions of **1** and **9** were over 90%. The data reported were an average of four or more independent samples, each sample being measured four times. The error limits in Tables III and IV refer to the standard deviation.

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Micellar Microviscosity of Ionic Surfactants under High Pressure†

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Abstract: The microviscosities of ionic micelles of sodium dodecylsulfate (SDS), hexadecyltrimethylammonium bromide (HDTBr), and hexadecyltrimethylammonium chloride (HDTCl) are estimated from the monomer–excimer ratio of 1,3-α-dinaphthylpropane (DNP) under high pressure (1 to 2610 bars). Excimer formation is inhibited with elevated pressure. The derived microviscosities (η of SDS, HDTBr, and HDTCl) are 12, 47, and 27 cP, respectively, at 25 °C, at atmospheric pressure. The η values increase with pressure from 27 cP (1 bar) to 101 cP (2610 bars) for HDTCl. Additions of sodium chloride, sodium sulfate, and ethanol to the surfactant solutions are found to generally decrease the η values. The intermolecular excimer formation of pyrene in surfactant solutions is retarded by application of high pressure. However, the excimer–monomer ratio of pyrene does not give values of micellar microviscosity that are consistent with those derived from the DNP method. The data on the pressure dependence of micellar microviscosity is consistent with the penetration of water into the interior of micelle cores.

Photophysical techniques afford very convenient and powerful methods for the investigation of the structures and properties of micellar solutions.[1] For example, the microviscosity experienced by the fluorophore associated with a micellar aggregate may be evaluated from the extent of excimer formation,[2,3] from the degree of fluorescence depolarization,[4] and from fluorescence fine spectra.[5] Among excimer methods, *intramolecular* excimer formation of bichromophores possesses the advantage that excimer emission is exclusively unimolecular and that statistical factors related to the probe distribution in the micelles may be ignored,[2] i.e., *intermolecular* excimer formation[2b,3] is a function of not only diffusional motion of the probes, but also the local probe concentration and probe distributions.

The macroscopic viscosity of liquid hydrocarbons is very sensitive to temperature and pressure,[6] whereas water viscosity is

† This paper is dedicated to George S. Hammond in commemoration of his 60th birthday.

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