0^0 level of the uncomplexed tetrazine following $6a^1$ excitation of the complex. The calculations also predict very little 0^0 complex emission following $16a^1$ excitation of the complex. In all cases these predictions and the experimentally observed results are in complete agreement.

Conclusions

This simple, one-parameter RRKM model is in semiquantitative agreement with all the static and time-resolved data for which comparison is possible. The detailed validity of this model can be unambigously tested only by direct time-resolved spectroscopic studies of both complexed and uncomplexed molecules in specific vibrational states.

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State-Selective Photochemistry of Singlet Oxygen Precursors: Kinetics and Wavelength Dependence of the Photodissociation of Anthracene Endoperoxides

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The photochemical behavior of the two isomeric endoperoxides (9,10-PMO_2 and 1,4-PMO_2) of 1,4-dimethyl-9,10-diphenylanthracene was found to differ in their kinetics and reaction efficiencies. Consistent with the work of Rigaudy et al. and Brauer et al. on a related endoperoxide we find that the generation of ${}^1O_2$ is wavelength dependent, occurring from upper excited singlet states of the endoperoxide, whereas bond cleavage of the O–O endoperoxide bond occurs principally from the lowest excited singlet and triplet states. Results of picosecond kinetics and absolute quantum yield measurements are discussed in terms of various concerted and nonconcerted mechanisms for the formation of ${}^1O_2$ and the anthracene fragment.

Introduction

Whether it is a state-dependent reaction of an intermediate or of an excited-state precursor, the observation of state-selective chemistry is important in the determination of reaction mechanisms. The case of wavelength-dependent photochemistry is particularly interesting since the initially prepared excited state places stringent constraints on the chemical decay pathway. As a general rule, organic photoreactions in solution do not occur efficiently from upper electronically excited states (S_n or T_n, where $n \geq 2$) due to the very rapid relaxation to the lowest excited state of the same symmetry (Kasha's rule).[1] The photochemical reactions of the 9,10- and the 1,4-endoperoxides[3,4] of anthracene are conspicuous exceptions to this general rule. For example, Rigaudy[3] first reported the wavelength dependence of product formation in the photochemistry of anthracene endoperoxides, and later Brauer et al.[4] convincingly demonstrated that the wavelength dependence results from a higher reactivity of upper singlet states (S_n, $n \geq 2$) toward fragmentation into the parent anthracene and molecular oxygen. Brauer et al.[4] also found that molecular oxygen was produced in its excited singlet state, thus demonstrating that the upper state reaction occurs adiabatically. Picosecond work on a 1,4-endoperoxide anthracene derivative also showed the adiabaticity of photofragmentation for upper excited singlet states by finding that the anthracene fragment was formed in its excited singlet state although through a minor dissociative route.[12] In addition to being of intrinsic interest because of its special status as an upper state, adiabatic process, the photochemistry of anthracene endoperoxides has attracted attention because of the possibility of correlating experiments with the theoretical calculations of Kearns and Khan,[5] who predicted the state-selective (S_1, O–O bond cleavage; S_2, concerted adiabatic cleavage of the C–O bonds) photochemistry of aromatic endoperoxides. Furthermore, the thermolyses of anthracene endoperoxides are exceptional in that singlet molecular oxygen, a species of wide chemical importance in its own right,[6] is produced in a chemiluminescent process.[7] Thus, since the anthracene endoperoxides possess unusual and intriguing ground- and excited-state behavior, it is of value to investigate and compare systematically the thermal chemistry and photochemistry for a selected set of structures. We report here an investigation of the chemical and physical properties of the excited electronic states of two isomeric endoperoxides of 1,4-dimethyl-9,10-diphenylanthracene: 9,10-PMO_2 and 1,4-PMO_2 (Scheme I), two substances whose thermal chemistry and thermochemical parameters have been established.[7a] The salient results of our photochemical studies are (1) the observation of different wavelength dependences of the photochemistry of 9,10-PMO_2 and 1,4-PMO_2, which is accounted for by the different reactivities of upper excited singlet π,π^* states (S_n, $n \geq 2$), (2) direct spectroscopic determination of the singlet molecular oxygen produced from the photolysis of 9,10-PMO_2 and 1,4-PMO_2 as well as direct spectroscopic measurement of the dynamics of formation of the parent anthracene (PM) from the photoexcited endoperoxide, and (3) spectroscopic kinetic evidence consistent with a

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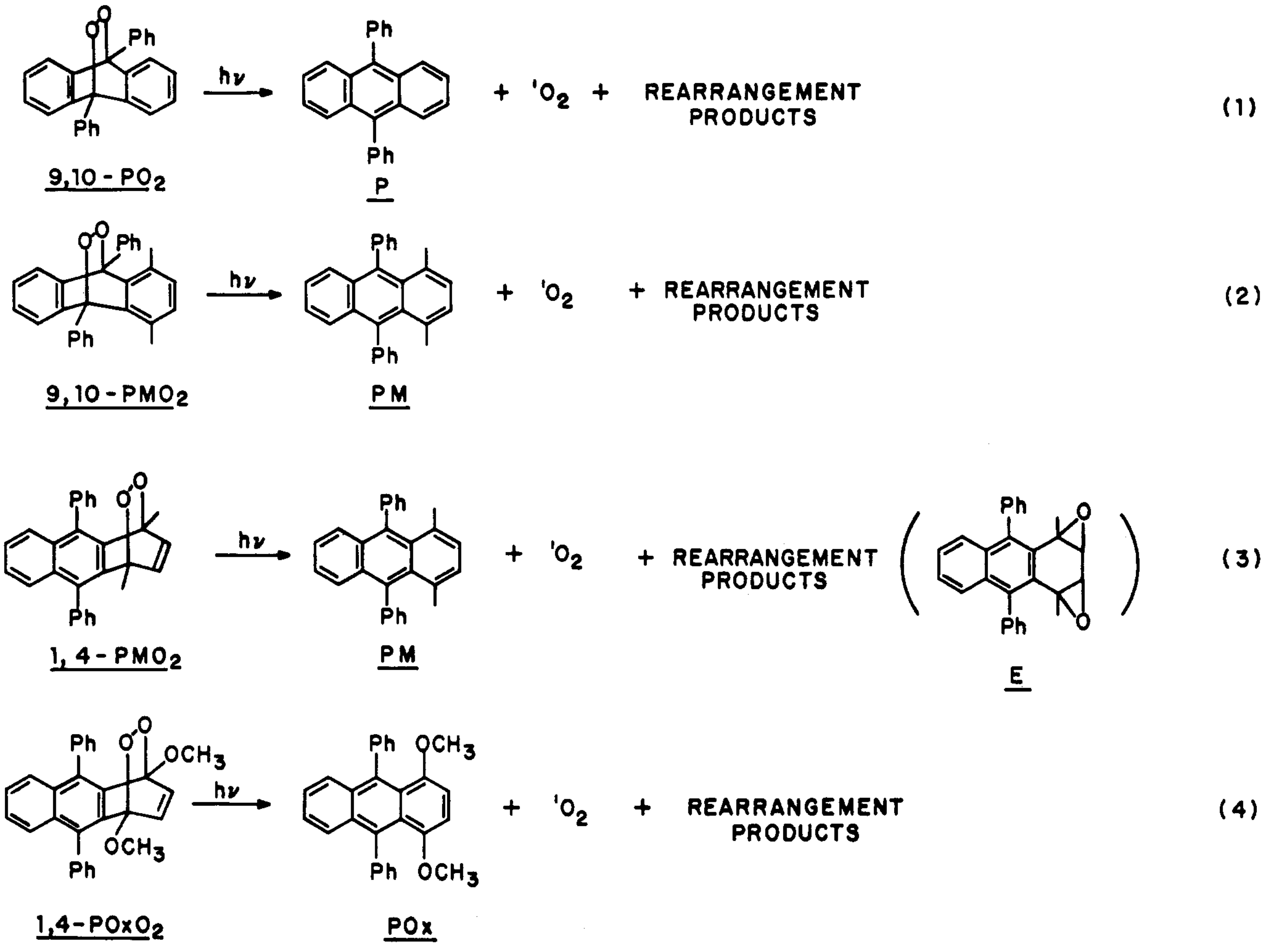
SCHEME I: Photochemical Reactions of Anthracene Endoperoxides



stepwise production of PM + $^1O_2$ via an intermediate (zwitterion or biradical).

Experimental Section

The laser apparatus and the two-pulse, pump-delayed-probe laser-induced fluorescence techniques have been described elsewhere.[12,13] In these experiments the excitation pulse is the fourth harmonic of a mode-locked Nd:YAG laser: $\lambda = 266$ nm, pulse width of 25–30 ps, energy per pulse ≤ 0.05 mJ, focused to approximately 2 mm^2, which is equivalent to approximately one photon per 10 endoperoxide molecules in the sampling region. The probing pulse is the third harmonic of the mode-locked Nd:YAG: $\lambda = 355$ nm, pulse width 25–30 ps, energy per pulse 0.2 mJ, focused to 4 mm^2. The samples were irradiated to less than 1% conversion to avoid photoproduct buildup. The system response was obtained by measuring the $S_1 \rightarrow S_n$ absorption of naphthalene in hexane at 355 nm following excitation at 266 nm, where the time constant for excited-state population was assumed to be ≤ 1 ps.

The singlet oxygen emission (1270 nm, $^1\Delta_g \rightarrow {}^3\Sigma_g$) was measured with an InSb photodiode detector and lock-in receiver.[11] Emission at 1270 nm was detected at right angles through a silicon disk (cutoff < 1000 nm) and a narrow band-pass interference filter (half bandwidth ~ 20 nm) with a cooled InSb photodiode (1 mm^2, 77 K, response < 0.5 s). The signal was amplified with a matched preamplifier (gain 10) and a Tektronix AM 502 differential amplifier (1 MHz, gain 100). The amplified signal was recorded and analyzed on a Tektronix 7912 programmable digitizer.

The quantum yield of $^1O_2$ formation was measured under steady-state irradiation conditions. In a typical experiment, a degassed sample of an endoperoxide was photolyzed with an arc lamp setup. Upon extended irradiation, the emission intensity at 1270 nm decreased due to loss of the endoperoxide. In order to minimize this effect, the lamp output was gated with a shutter to give short bursts (70 ms for 1,4-PMO$_2$ and 500 ms for 9,10-PMO$_2$) of light. The transient $^1O_2$ signal was monitored at right angles with a room-temperature PbS detector using the same filters as described above. The signal was amplified with a Tektronix AM 502 differential amplifier and recorded on a Tracor Northern 7210 multichannel analyzer in a slow-sweep mode. At least eight transients were recorded per sweep. After a single sweep, the concentration of anthracene was measured by fluorescence and conversions were generally <10%.

Endoperoxides 1,4-PMO$_2$ and 9,10-PMO$_2$ were prepared by photolysis of a methylene chloride solution of PM (1 g per 100 mL) and methylene blue (10 mg) under continuous oxygen bubbling. The reaction was essentially complete after 4 h (crude product ratio 9,10-PMO$_2$/1,4-PMO$_2$ was 3/1). The solvent was removed and the remaining solid was chromatographed on silica gel with CH_2Cl_2/hexane eluent. The separated endoperoxides were further purified by preparative thin-layer chromatography (Silica gel, 1:1 CH_2Cl_2:hexane) and then recrystallized from hexane. Fluorescence measurements indicated that there was less than 0.01% of PM present in the purified samples. The product yield measurements were done by steady-state lamp irradiation and gas-phase chromatography analysis.[8]

Results

Quantum Yield Measurements. As a first step toward understanding the broad issue of the competing pathways for energy relaxation in endoperoxides as well as how this competition

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TABLE I: Absolute Quantum Yields for the Formation of Anthracene and Singlet Oxygen from Photolysis of Endoperoxides 9,10-PMO$_2$, 1,4-PMO$_2$, and 9,10-PO$_2$ at 254 nm in Argon-Purged Acetonitrile

endoperoxide	Φ_{abs}	$^1O_2$
9,10-PO$_2$	0.28 ± 0.03[a]	0.22 ± 0.06
9,10-PMO$_2$	0.31 ± 0.07	0.36 ± 0.10
1,4-PMO$_2$	0.8 ± 0.1[b]	0.7 ± 0.2

[a] From ref 4. [b] Obtained at 266 nm with ferrioxalate actinometry after photolysis of 1,4-PMO$_2$ with the fourth harmonic of a Nd:YAG laser.

eventually expresses itself in the distribution of final products, it is necessary to determine the primary photoproducts, their relative yield, and the conditions needed to generate them. Steady-state irradiation of 9,10-PMO$_2$ at 254 nm in acetonitrile yields about 60% of an anthracene moiety (PM),[8] in addition to several other products expected from cleavage of the O–O bond of the peroxide.[3] Photolysis of the isomer 1,4-PMO$_2$ under the same conditions yields[8] only PM (ca. 60%) plus a second product assigned to the diepoxide structure E (see Scheme I).[3]

Although both 9,10-PMO$_2$ and 1,4-PMO$_2$ were found to decompose under conditions of triplet photosensitization (benzophenone), the parent anthracene (PM) could not be detected even at high (ca. 70%) conversion. It is therefore concluded that the excited triplet state does not play a role in the direct formation of PM and thus O$_2$. Rather, the triplet-state reaction probably involves O–O bond rupture, which is consistent with the theoretical picture presented by Kearns and Khan.[5] At issue now is what state or states of the endoperoxide possessing singlet-state multiplicity are reponsible for the production of the parent anthracene as well as the efficiency of generation.

To determine the efficiency of the photoreaction leading to anthracene and thus to assess the manner in which the excited state can dispose its energy, the relative quantum yields for formation of PM were measured. The quantum yields were put on an absolute basis by comparison with 9,10-PO$_2$, which has been shown to possess a quantum yield of 0.28 ± 0.03 for irradiation ($\lambda < 294$ nm) in *n*-heptane.[4a] The data are summarized in Table I.

From these results it is evident that upon 254-nm excitation the relative efficiency of anthracene formation is less than unity and that it is approximately 3 times greater for the 1,4-endoperoxide compared to the 9,10-endoperoxide. The values for the quantum yields of anthracene production indicate that there is a competition between the photochemical production of PM and other modes of energy relaxation. The quantum yield measurement at a fixed excitation wavelength, however, does not allow the identification of the specific electronic states from which the photochemical reaction leading to anthracene occurs. Namely, the direct production of PM does not necessarily have to arise from the initially prepared state, since the initial excited state may decay into a lower electronic state from which the chemical reaction occurs. To characterize the particular excited state(s) of the endoperoxide yield of anthracene and molecular oxygen, a study of the quantum yield of the anthracene (PM) product formation as a function of excitation wavelength was undertaken.

The wavelength dependence for photodecomposition of 1,4-PMO$_2$ and 9,10-PMO$_2$ was determined by measuring the fraction of anthracene PM in the photoproducts. The results are shown graphically in Figures 1 and 2. The relative quantum yield measurement at 254 nm for 9,10-PMO$_2$ and the reference compound 9,10-PO$_2$ shows nearly identical behavior as a function of wavelength. On the other hand, the endoperoxide 1,4-PMO$_2$ was found to have a different wavelength dependence. Although the formation of PM increases with decreasing excitation wavelength, no limiting plateau region is reached for 1,4-PMO$_2$ as is found for 9,10-PO$_2$ and 9,10-PMO$_2$.

In summary, it is found that 9,10-PMO$_2$ is essentially equivalent to 9,10-PO$_2$ in terms of the quantum yield of anthracene production and its dependence on excitation wavelength but that 1,4-PMO$_2$ has a larger quantum yield of anthracene as well as a different wavelength dependence of the quantum yield. Consideration of the marked difference of the wavelength dependence of PM formation between the 1,4- and 9,10-endoperoxides leads to the question of whether this difference could manifest itself in the kinetics of product formation. This is an important issue since the case in question pertains to a situation in which the same photoproducts (i.e., PM and O$_2$) are produced from two structurally different precursor molecules that also exhibit significantly different wavelength dependences of photodissociation.

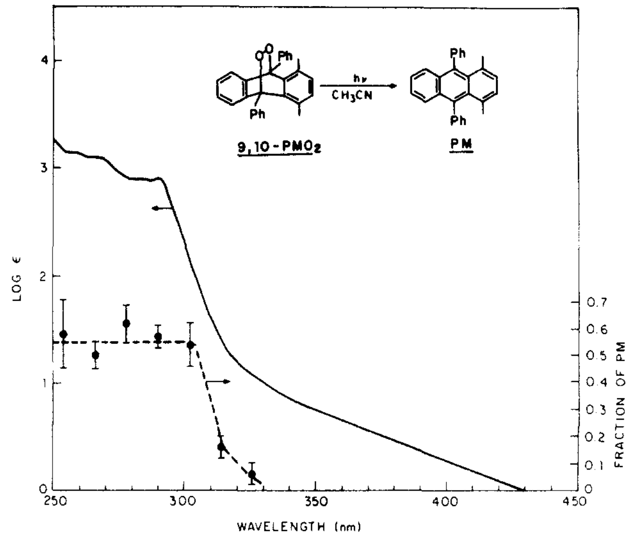

Figure 1. Wavelength dependence of the photodissociation of 9,10-PMO$_2$. Comparison of the electronic absorption spectrum of 9,10-PMO$_2$ to the fractional yield of PM produced upon photolysis of 9,10-PMO$_2$ as a function of excitation wavelength, using acetonitrile as solvent at ambient temperature.

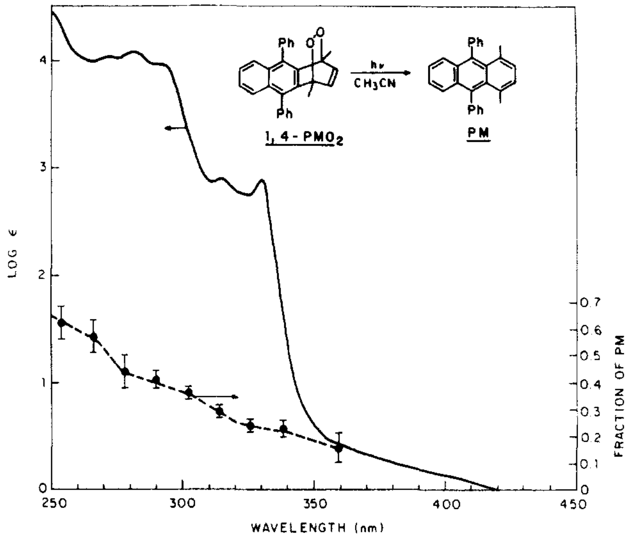

Figure 2. Wavelength dependence of the photodissociation of 1,4-PMO$_2$. Comparison of the electronic absorption spectrum of 1,4-PMO$_2$ to the fractional yield of PM produced upon photolysis of 1,4-PMO$_2$ as a function of excitation wavelength, using acetonitrile as solvent at ambient temperature.

Picosecond Measurements. To follow the kinetics of the growth of PM following photodissociation of the endoperoxide precursor, a laser-induced fluorescence (LIF) technique was used with 266-nm pump and 355-nm time-delayed probe pulses. With the $S_1 \rightarrow S_n$ excited-state absorption of naphthalene to obtain the system response, a best fit to the LIF data for the kinetics of PM generation is obtained for an exponential rise time of 50 ± 15 ps for the 1,4-PMO$_2$ precursor and 75 ± 20 ps for the 9,10-PMO$_2$ precursor.

Although a triplet pathway for formation of the observed products is energetically possible, no triplet–triplet absorption from anthracene PM was observed immediately after photodissociation of 9,10-PMO$_2$ or 1,4-PMO$_2$.[12] With a conservative value for the triplet absorption of PM, based on values for similar anthracenes,[9] and with the triplet of 9-fluorene[10] as a standard, the picosecond measurements set an upper limit of 10% for formation of the triplet of PM. Further arguments against the formation of the triplet can be made from the high and identical (within experimental error) yields of PM and $^1O_2$, vide infra.

Spectroscopic Singlet Oxygen Measurements. Since an electronically excited singlet endoperoxide produces PM in its singlet state, spin conservation rules suggest that molecular oxygen would also be produced with singlet spin multiplicity. This situation would apply either for a concerted photofragmentation mechanism or for the case of a sequential bond rupture process where the sequence of intermediary steps is faster than the rate of spin-orbit and/or hyperfine interactions that would be required to change the spin angular momentum of the photoproducts from that of the initial precursor state. The spectroscopic identification of singlet molecular oxygen arising from the photodissociation of endoperoxides would be highly relevant in terms of directly showing the adiabaticity of the process. Knowledge also of its quantum yield of formation relative to anthracene formation would provide important details on the mechanism of the photofragmentation.

Brauer et al.[4] have demonstrated via chemical trapping experiments that photolysis of 9,10-PO_2 by excitation of S_2 produces equal molar quantities of P and singlet molecular oxygen ($^1O_2$). In our experiments we find that the characteristic emission of $^1O_2$ (1270 nm, $^1\Delta_g \rightarrow {}^1\Sigma_g$) is produced by pulsed-laser excitation of 9,10-PO_2 or 9,10-PMO_2 at 266 nm in acetonitrile. The observed $^1O_2$ lifetime of 54 ± 9 μs is in excellent agreement with values reported in the literature.[11] Measurements were made under degassed conditions in order to avoid secondary production of $^1O_2$.

The efficiencies of $^1O_2$ formation from 1,4-PMO_2 and 9,10-PMO_2 were measured under steady-state conditions ($\lambda < 300$ nm). The 1270-nm emission of $^1O_2$ was integrated and compared to the 1270-nm emission produced by steady-state excitation of 9,10-PO_2 as a standard.[4] Quantitative measurements were made in 1,1,2-trichlorotrifluoroethane, since an excellent signal-to-noise ratio is obtained because of the long (ca. 42 ms) lifetime of $^1O_2$ in this solvent. The relative yield of $^1O_2$ was determined by comparing the integrated emission intensity of $^1O_2$ upon photolysis of the endoperoxide with that obtained from photoexcitation of a $^1O_2$ sensitizer (benzophenone or naphthalene) with known triplet yield under the same conditions. The results are summarized in Table I.

Discussion

The electronic spectrum and steady-state photochemistry of 9,10-PMO_2 parallels that of 9,10-PO_2 in all significant respects. We therefore expect the interpretation of wavelength effects and adiabatic characteristics as given by Brauer et al.[4] for 9,10-PO_2 to be directly applicable to the photochemistry of 9,10-PMO_2. The electronic spectra of both 9,10-PO_2 and 9,10-PMO_2 show at lowest energies (320–430 nm, Figure 1) a broad, weak band ($\epsilon \sim 1$–10 M^{-1} cm^{-1}), attributable to a $\pi^*_{00} \rightarrow \sigma^*_{00}$ transition of the peroxide bond.[5] The next higher energy band, which commences at wavelengths less than ca. 310 nm, maximizes at ca. 255 nm with an extinction of ca. 10^3 M^{-1} cm^{-1} and is attributable to a π, π^* transition, where π, π^* refers to the optical transition of the aromatic moiety.[4]

Kearns and Khan[5] showed that the concerted reaction[14] of an endoperoxide to produce $^1O_2$, based on a state correlation analysis, should not originate in $S_1(\pi^*_{00}, \sigma^*_{00})$ or $T_1(\pi^*_{00}, \sigma^*_{00})$ because these states must overcome energy barriers. On the other hand, the state correlation analysis predicted correlation of the upper excited singlet $S_2(\pi, \pi^*)$ exothermically and adiabatically to $^1O_2$ without energy barriers. The same state correlation diagram predicts that $S_1(\pi^*_{00}, \sigma^*_{00})$ or $T_1(\pi^*_{00}, \sigma^*_{00})$ should undergo homolytic rupture of the peroxide bond, a process facilitated by electron excitation into a σ^*_{00} orbital. Indeed, as predicted by the Kearns and Khan analysis $S_0 \rightarrow S_2$ excitation of 9,10-anthracene endoperoxides generally leads to formation of $^1O_2$ and the parent anthracene in good yield, whereas $S_0 \rightarrow S_1$ excitation or sensitized excitation of T_1 leads to products derived from the cleavage of the O–O bond. Since for 9,10-substituted endoperoxides the quantum yield of anthracene generally is constant[4] in the wavelength range 250–300 nm, it was concluded that only one electronic state (S_2) is photochemically active in this wavelength range. The absence of significant intersystem crossing in this wavelength range is consistent with the failure to observe triplet anthracene in the picosecond experiments. Brauer et al.[4] have shown that the quantum yield of anthracene and $^1O_2$ generation is generally wavelength independent for 9,10-anthracene endoperoxides in the range of $S_0 \rightarrow S_n$ ($n \geq 2$) excitation and generally falls off sharply as the region corresponding to $S_0 \rightarrow S_1$ excitation is approached. The results of Figure 1 are in complete accord with these results.

At the completion of this research the steady-state photochemistry of 1,4-PMO_2 did not have a direct analogy in the literature. Recently, Brauer et al. have reported[4c] the steady-state photolysis of a 1,4-dimethoxyanthracene endoperoxide (1,4-$POXO_2$). Some notable features relevant to our results with 1,4-PMO_2 are (1) S_2 excitation leads exclusively to fragmentation products, (2) the quantum yield for fragmentation is considerably higher (ca. 0.80) for the 1,4-$POXO_2$ system, and (3) the quantum yields for photofragmentation are not constant in the high-energy region. Our results with 1,4-PMO_2 also show a higher quantum efficiency (Table I) relative to that for 9,10-PMO_2 and a clear increase in the quantum yield as a function of excitation energy in the high-energy wavelength region 250–350 nm. In order to understand the observed wavelength dependence on the quantum yield that is unique to a given endoperoxide derivative, it is necessary to ascertain what state(s) are active in the photochemical process. Thus, a comparison of the quantum yield of photofragmentation with the absorption spectrum can provide an indication of the active states involved.

The absorption spectrum of 1,4-PMO_2 shows a characteristic $S_0 \rightarrow S_1$ ($\pi^*_{00}, \sigma^*_{00}$) absorption in the 350–400-nm region. A strong absorption, absent in 9,10-PMO_2, begins at ca. 350 nm, maximizes at 340 nm ($\epsilon \sim 10^3$ M^{-1} cm^{-1}), and has been assigned to $S_0 \rightarrow S_2(\pi, \pi^*)$ absorption of the naphthalene chromophore.[4] A still stronger band commences at about 300 nm, maximizes at ca. 285 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}), and is assigned to $S_0 \rightarrow S_3(\pi, \pi^*)$ absorption of the naphthalene chromophore.[4c] The lack of a clearly definable plateau region for 1,4-PMO_2 (Figure 2) suggests that more than one state contributes to the photofragmentation process for wavelengths less than 350 nm.[4d] In contrast the quantum yield for 9,10-PMO_2 and 9,10-PO_2 has a definite plateau once the $S_2(\pi, \pi^*)$ is reached, i.e., from 300 to 250 nm. A comparison (Figure 4) of the absorption spectra for 9,10-PMO_2 and 1,4-PMO_2 supports the view that for the 9,10-PMO_2 only a single electronic state (S_2) is in the region of 300–250 nm whereas for the 1,4-PMO_2 the spectrum shows that there is at least one more electronic state, i.e., the $S_3(\pi, \pi^*)$ state.

Thus, although the steady-state photochemistries of 9,10-PMO_2 and 1,4-PMO_2 show qualitatively similar behavior in terms of their quantum dependence on excitation wavelength, a quantitative difference is observed in the magnitude of the upper state reactivity (1,4-PMO_2 > 9,10-PMO_2) and in the detailed behavior of upper state reactivity as a function of excitation energy (Figures 1 and 2). It should be noted that the absolute quantum yield values of anthracene production are equal (Figures 1 and 2) for both the 1,4-PMO_2 and 9,10-PMO_2 precursors when they are excited to their $S_2(\pi, \pi^*)$ states. Excitation of the 1,4-PMO_2 at 285 nm and below excites the $S_3(\pi, \pi^*)$ state, which gives a higher quantum yield of anthracene production.

From our steady-state results and those of Brauer et al.,[4] the following general trends for anthracene endoperoxides are indicated:

1. Excitation of $S_1(\pi^*_{00}, \sigma^*_{00})$ or $T_1(\pi^*_{00}, \sigma^*_{00})$ of either 9,10- or 1,4-endoperoxides results in O–O bond cleavage followed by rearrangements.

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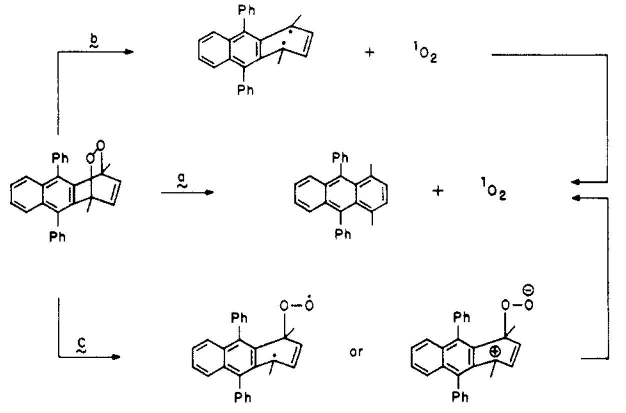
[14] This one-step sequence is commonly referred to as a retrocycloaddition reaction.

SCHEME II: Upper Excited π,π^* State Photofragmentation of Endoperoxides, Using 1,4-PMO$_2$ as an Example: (a) Concerted Mechanism; (b) Dual Bond Cleavage Producing $^1O_2$ and Isomeric Anthracene; (c) Sequential Bond Rupture Involving a Biradical or Zwitterionic Intermediate



2. Excitation of $S_2(\pi, \pi^*)$ of either 9,10- or 1,4-endoperoxides results in upper state fragmentation to the parent anthracene and singlet molecular oxygen which is in competition with energy relaxation to S_1.

3. The efficiencies of excitation to $S_2(\pi, \pi^*)$ for the 1,4-endoperoxides and 9,10-endoperoxides are equal. For the 1,4-endoperoxide, excitation to the $S_3(\pi, \pi^*)$ state is more efficient in $^1O_2$ formation than excitation to the $S_2(\pi, \pi^*)$ state. This increase of the efficiency upon excitation of S_3 means that reaction does occur in the S_3 state.

Some issues raised by the dynamic measurements are as follows: What is the basis for the differing dynamics of the 1,4- and 9,10-endoperoxides? Is the anthracene fragment produced in a concerted process or is there an intermediate species between the excited precursor and anthracene?

Scheme II depicts three routes for upper excited-state photofragmentation of endoperoxides, using 1,4-PMO$_2$ as the example. Path a represents a concerted fragmentation into the ground-state anthracene and $^1O_2$, path b involves the very rapid rupture of both C–O bonds to give $^1O_2$ and an isomeric form of anthracene, and path c represents a stepwise fragmentation process with cleavage of a C–O bond to form a biradical or a zwitterionic intermediate as the initial step.

If the concerted mechanism is the correct one, then an explanation of the origin of the observed 50 and 75 ps rise times is needed. One possibility is that a vibrationally hot ground-state anthracene fragment is produced that for these high vibrational levels absorbs only weakly at the probe wavelength. The hot anthracene fragment must relax to the lower vibrational levels for absorption to occur and the observed LIF rise times are due to the vibrational relaxation process. For a large molecule in condensed media such a slow vibrational relaxation would not be expected and is unprecedented.

A second possibility consistent with a concerted mechanism would have the vibronic relaxation of the photoexcited endoperoxide from its S_n ($n \geq 2$) states be the source of the 50 and 75 ps rise times found for the 1,4-PMO$_2$ and 9,10-PMO$_2$ precursors. The difficulty with this explanation is that for large organic molecules the internal conversion rates are generally much more rapid than 50 or 75 ps. Experimental evidence suggests that the deactivation of the initially prepared state S_n ($n \geq 2$) of the endoperoxide is extremely rapid. It has been found that pulsed-laser excitation of 1,4-PMO$_2$ at 266 nm yields an excited singlet anthracene (^{1*}PM) in less than 5 ps.[12a] Although the product of ^{1*}PM was shown to be a minor decay pathway ($\leq 1\%$), it would follow that the kinetics of formation of the minor channel (^{1*}PM) and the more important one yielding ^{1}PM would be the same if they originate from a common state. If, however, the 50-ps growth time results primarily from relaxation from states different from the initially prepared state, the latter being the one that is probably the state leading to the ^{1*}PM decay route, then the 5- and 50-ps decay times are compatible.

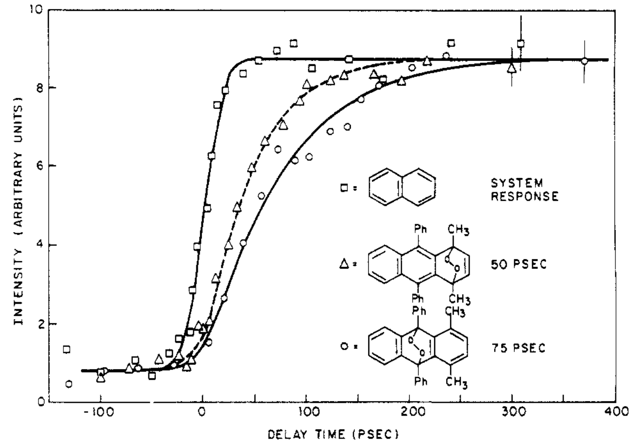


Figure 3. Growth kinetics of PM following picosecond laser photolysis at 266 nm of 9,10-PMO$_2$ (○) and 1,4-PMO$_2$ (△) in acetonitrile at ambient temperature. System response (□) obtained from $S_1 \rightarrow S_n$ absorption of naphthalene.

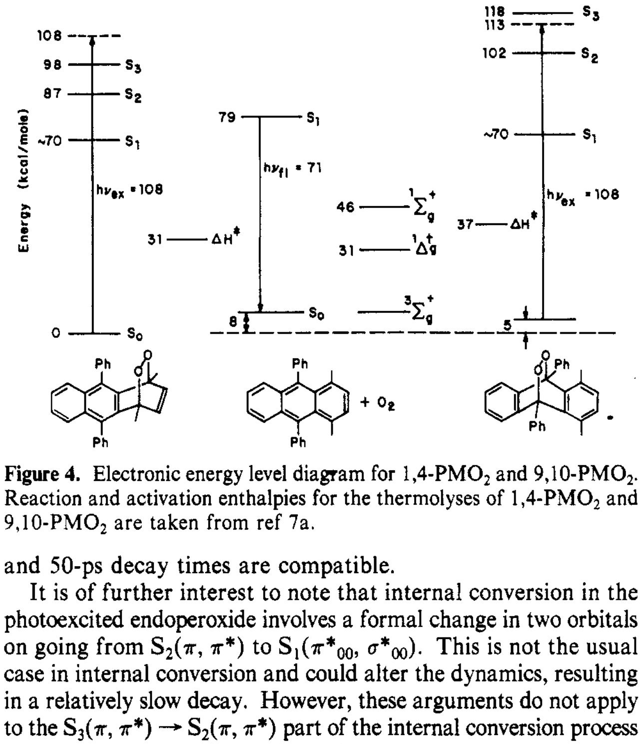


Figure 4. Electronic energy level diagram for 1,4-PMO$_2$ and 9,10-PMO$_2$. Reaction and activation enthalpies for the thermolyses of 1,4-PMO$_2$ and 9,10-PMO$_2$ are taken from ref 7a.

It is of further interest to note that internal conversion in the photoexcited endoperoxide involves a formal change in two orbitals on going from $S_2(\pi, \pi^*)$ to $S_1(\pi^*_{00}, \sigma^*_{00})$. This is not the usual case in internal conversion and could alter the dynamics, resulting in a relatively slow decay. However, these arguments do not apply to the $S_3(\pi, \pi^*) \rightarrow S_2(\pi, \pi^*)$ part of the internal conversion process for the 1,4-PMO$_2$ since only π, π^* states are involved. The rise should be extremely rapid (<5 ps) for an $S_3(\pi, \pi^*) \rightarrow S_2(\pi, \pi^*)$ energy relaxation. Since the quantum yield of PM is higher for excitation of S_3, Figure 2, than for S_2 we deduce that reaction is occurring in S_3 and furthermore must occur competitively with the rapid $S_3 \rightarrow S_2$ relaxation. If this was not the case, then the efficiency of $^1O_2$ product on S_3 excitation would be the same as on excitation to S_2, which is contrary to what is observed.

An additional point to note for the 1,4-PMO$_2$ is that if both C–O bonds were ruptured simultaneously, i.e., concerted, then the LIF detection of the anthracene fragment should have yielded a rise time that was limited by the system response. This was not the case, as shown in Figure 3. For the 9,10-PMO$_2$ on the other hand, the highest energy state we are exciting at 266 nm is the $S_2(\pi, \pi^*)$ state. Since the population of two orbitals are changed in the $S_2 \rightarrow S_1$ transition, a slower internal conversion rate to the $S_1(\pi^*_{00}, \sigma^*_{00})$ state is possible. Thus a concerted mechanism could be consistent with the quantum yield and slow rise time (75 ps) for the 9,10-PMO$_2$.

For the mechanism indicated as path b there is a "simultaneous" rupture of both C–O bonds as in path a. However, rather than yielding $^1O_2$ and a ground-state anthracene fragment an isomeric anthracene fragment, shown as a biradical in Scheme II, is produced. The relaxation of this transient, which is essentially an

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anthracene valence isomer structure, to the ground-state anthracene fragment could be responsible for the observed rise time of 50 ps. One might ask why we do not specify that this dual C–O bond rupture path is a concerted process. For the purposes of this paper we do not call this mechanism a concerted one since the electronic structure of the intermediate is unknown and therefore we cannot determine whether orbital symmetry is conserved in producing the anthracene valence isomer fragment.

In contrast with mechanism a, the stepwise fragmentation mechanism as well as mechanism b does not require any special explanation of a slow internal conversion nor the fast decay process (<5 ps) leading to ^{1*}PM. For the stepwise mechanism, path c, the 50 or 75 ps appearance time of the ground-state anthracene fragment would be determined by the kinetics of the decay of the broken bond intermediate. The internal conversion dynamics in the precursor would not have to be slow and would be consistent as well with the (<5 ps) appearance time of ^{1*}PM. The results do not, however, define the structure of the intermediate, which may be a biradical or a zwitterion. On the basis of singlet oxygen yields, magnetic field effects, and activation parameters, the thermolysis of 9,10-PMO$_2$ is proposed to proceed via a biradical mechanism, whereas the thermolysis of 1,4-PMO$_2$ is proposed to proceed via a concerted mechanism.[7] If a biradical is involved in the upper state photochemistry of 9,10-PMO$_2$, it is different (perhaps being an excited-state biradical) from that produced in the thermolysis of this peroxide. For the thermolysis the lifetime of the biradical must be on the order of nanoseconds, which does not correspond with the 50–75 ps intermediate observed in the photochemical process.

Conclusion

The comparative photochemistry of 1,4-PMO$_2$ and 9,10-PMO$_2$ has revealed qualitative similarities but quantitative differences. Both endoperoxides display wavelength-dependent product formation and quantum efficiencies that are explainable on the basis of different reactivities of their S$_1$(π^*_{OO}, σ^*_{OO}), S$_2$(π, π^*) and S$_3$(π, π^*) states. Both endoperoxides produce PM and singlet molecular oxygen on excitation to their π, π^* states. Although a short-lived chemical intermediate (path c) or a dual bond cleavage mechanism (path b) is consistent with the wavelength quantum yield and kinetics measurements, a concerted reaction (path a) cannot be ruled out. For this latter mechanism a surprisingly slow internal conversion rate from the endoperoxide excited π, π^* state is required to be consistent with kinetic and quantum yield data.

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Picosecond Time-Resolved Fluorescence Spectra of Ethidium Bromide: Evidence for a Nonactivated Reaction

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We have measured the fluorescence spectrum of ethidium bromide dissolved in both glycerol and water and intercalated into DNA following excitation by a 30-ps laser pulse. The streak camera based spectrometer allows approximately 20-ps time resolution. Time-dependent spectral changes of excited singlet ethidium bromide in water and DNA are very small, but ethidium bromide in glycerol shows a large red shift which is nonexponential in time and occurs on a subnanosecond time scale. This change can be attributed in part to phenyl group rotation with respect to the phenanthridium ring in the excited state. Such a reaction may not be activated but forced by the bond torsion against the viscous solvent. The fast rate and low activation energy of this reaction suggest that it is not controlled by the static viscosity of the glycerol solution, but by the high-frequency component of the frictional forces of the viscous solvent.

Introduction

Picosecond laser technology provides useful probes of molecular relaxation in solvents. Many such phenomena are known: cage effects in geminate recombination,[1] electron solvation,[2] and the rotational motion of small molecules[3] are examples. Of particular recent interest has been molecular isomerization,[4] such as the cis–trans isomerization of stilbene[5,6] or isomerization in cyanine dyes.[7,8] Although other techniques such as NMR have been employed,[9] most isomerization studies are conducted with picosecond fluorescence or absorption techniques. The fluorescence techniques rely on quenching of fluorescence upon isomerization. The absorption techniques are somewhat more powerful, because the ground-state reverse isomerization may also be studied.

Considerable interest centers around the relationship between isomerization rates and solvent viscosity. These isomerizations are viewed as activated processes which proceed across a barrier. This barrier differs from the classical barrier of transition-state theory by possessing both an activation (potential) energy and friction. The viscosity determines the friction at the barrier. Both excessively low and excessively high viscosities tend to hinder the isomerization; high viscosities decelerate the rate of crossing at the top of the barrier, while low viscosities provide insufficient thermal coupling with the solution for activation to proceed efficiently. The frictional force is not determined by the static viscosity alone, and much work has gone into studying dynamic frictional forces.[6]

Multichannel signal acquisition is another technology that has had a significant recent impact on our understanding of molecular

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