PICOSECOND KINETICS OF STATE-SELECTIVE SINGLET OXYGEN PRODUCING PHOTOCHEMISTRY OF AROMATIC ENDOPEROXIDES

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Received 7 June 1989; in final form 24 July 1989

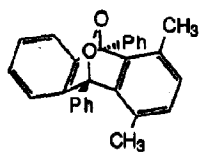
Picosecond measurements show that the photo-fragmentation of anthracene endoperoxides leading to the anthracene moiety and singlet oxygen does not occur in a single step, but involves a short-lived intermediate. The upper excited state dual bond dissociation kinetics of the endoperoxides of 9,10-diphenylanthracene (9,10-DPA-O_2) and of 9-phenylanthracene (9,10-PA-O_2) were measured. For 9,10-DPA-O_2 the ground state aromatic appears in 95 ± 10 ps, whereas for 9,10-PA-O_2 it appears in 60 ± 7 ps. The results are consistent with our earlier proposed mechanism for the dissociation from the upper excited singlet states of isomers of the anthracene endoperoxides.

1. Introduction

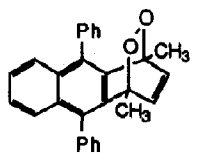
The observation of electronic state selective chemistry provides valuable insight into the nature of chemical reactions. For cases in which the photochemistry depends on the wavelength of the irradiating light the initially excited state not only determines the pathway of a chemical reaction but also requires the existence of an extremely efficient chemical reaction to compete with rapid energy relaxation processes.

Aromatic endoperoxides are compounds known to undergo wavelength-dependent photochemistry [1–11]. Steady state quantum yield measurements of the products showed that exciting into S_1 gives products derived from O–O rupture, but excitation to higher states gives $^1O_2$ and the anthracene moiety, as shown in scheme 1. We have extended our studies of these molecules, characterized by an O–O peroxide bridge, to better understand the nature of the photofragmentation process and its dependence on the wavelength of the exciting light. We were also motivated by the importance of these compounds as a useful source of singlet molecular oxygen, $^1O_2$, an active species in the degradation of chemical and biological substances and as an energy pump for the high-powered iodine laser [12].

A crucial issue in describing the observed chemistry following photoexcitation is to know the chemical species first produced. Does the photodissociation lead directly to the expected singlet oxygen intermediate, or is it preceded by other intermediates which could themselves undergo reactions other than the one leading to the anticipated intermediate? It was widely assumed that photodissociation of endoperoxides involved the simultaneous rupture of both C–O bonds leading directly to $^1O_2$ and the ground state aromatic fragment [13–15]. We have found [11,16] that this is not the case for 1,4-dimethyl-9,10-diphenylanthracene endoperoxides (DMDPA-O_2) but that there is an earlier step in the process, as shown in scheme 2. Important new experimental evidence for the two-step mechanism was also recently found for the upper excited state de-



9,10-DMDPA-O_2



1,4-DMDPA-O_2

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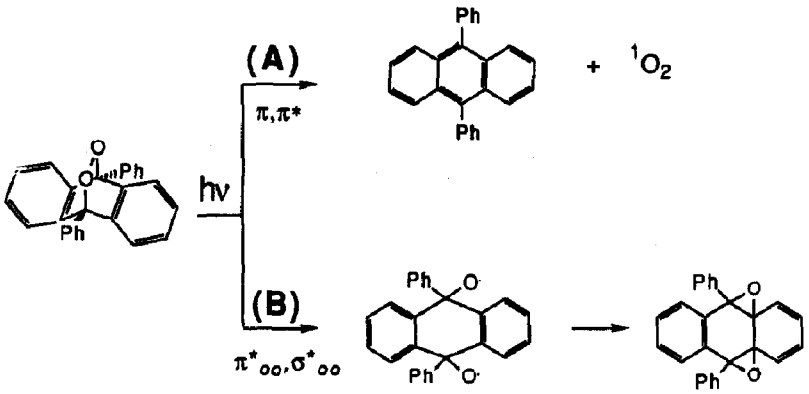


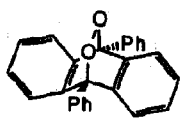
Scheme 1. State selective photodecomposition pathways for aromatic endoperoxides: (A) $S_n(n \geq 2)$ excited state decay to produce $^1O_2$ and the aromatic moiety, and (B) S_1 excited state decay via O–O bond rupture.

$$AO_2 \xrightarrow{h\nu} (AO_2)^* \xrightarrow{<5\,ps} [\text{intermediate}] \xrightarrow{50-100\,ps} {}^1O_2 + A$$

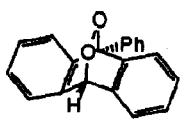
Scheme 2. Upper excited state (S_n, $n \geq 2$) photodecomposition of anthracene endoperoxides (AO_2).

composition of other aromatic endoperoxides as well [17,18].

To extend the generality of our results on the anthracene endoperoxide isomers we measured the formation kinetics of the aromatic moiety for phenyl substituted derivatives of the 9,10-anthracene endoperoxide. In particular we examined the 9,10-endoperoxide but without the methyl groups in the 1,4 positions, i.e. 9,10-DPA-O_2. The known wavelength dependence of this anthracene derivative is similar to the isomer 9,10-DMDPA-O_2, which we previously studied. We wish to establish whether the kinetics are the same and if so thereby establish a relationship between the observed electronic spectra and the kinetics of dissociation. Furthermore in order to better understand the nature of the photofragmentation process, its relation to the structure of the endoperoxide, and the dependence of the photodissociation pathways on the excitation wavelength we examined the 9-phenylanthracene derivative (9,10-PA-O_2).



9,10-DPA-O_2



9,10-PA-O_2

2. Results and discussion

Direct observation of the kinetics of anthracene formation following UV laser photodecomposition of endoperoxides 9,10-DPA-O_2 and 9,10-PA-O_2 was accomplished using the laser-induced fluorescence (LIF) method [11]. The experiment consisted of irradiation of a flowed, deoxygenated acetonitrile solution of the endoperoxide ($(0.8-1)\times10^{-3}$ M) with a picosecond laser pulse at 266 nm from a passively mode-locked Nd:YAG laser (25–30 ps fwhm, <0.01 mJ). The formation rate of the anthracene derivative was monitored by laser-induced fluorescence using a weak probe pulse at 355 nm at variable time delays. The results of the picosecond dynamic measurements are shown in fig. 1.

Using the measured system response a best fit to the LIF data was obtained for an exponential rise-time of 95 ± 10 ps for 9,10-DPA-O_2 and 60 ± 7 ps for 9,10-PA-O_2. These experiments demonstrate that the formation of the parent hydrocarbon proceeds at a non-instantaneous rate following photoexcitation.

Of special importance in endoperoxide photochemistry is the dependence of the product yields on excitation wavelength. Previous investigations [2,3] found for 9,10-DPA-O_2 that the fraction of anthracene in the photoproducts depended on the irradiating wavelength. Excitation into the $S_0 \rightarrow S_1$ ($\pi^*_{OO}, \sigma^*_{OO}$) band results in predominant formation of the products derived from the cleavage of the O–O bond (diepoxides, and secondary rearrangements,

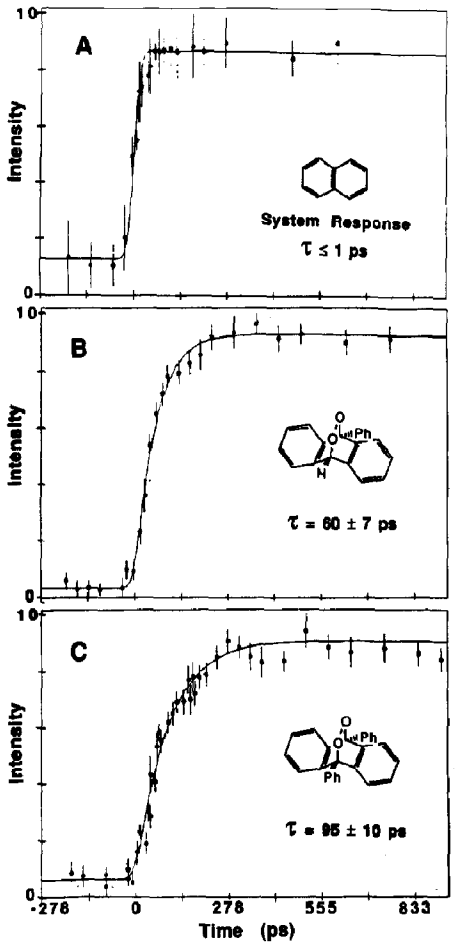


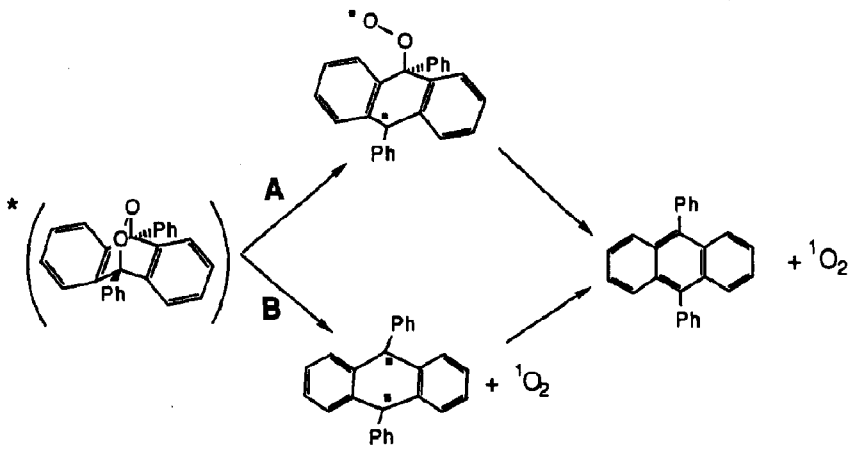
Fig. 1. (A) System response, obtained from $S_1 \rightarrow S_n$ absorption of naphthalene; (B) formation kinetics of 9-phenylanthracene following picosecond laser irradiation at 266 nm of 9,10-PA-O_2 in acetonitrile at ambient temperature; (C) formation kinetics of 9,10-diphenylanthracene following picosecond laser irradiation at 266 nm of 9,10-DPA-O_2 in acetonitrile at ambient temperature.

etc.). The absorption at wavelengths less than 294 nm ($\epsilon = 10^3$–10^4 M^{-1} cm^{-1}) corresponds to the $S_0 \rightarrow S_2$ (π, π^*) transition. Irradiation into this band resulted in predominant formation of 9,10-DPA and $^1O_2$. The yield of these two products was constant down to 254 nm. These results indicate that photofragmentation of 9,10-DPA-O_2, to produce 9,10-DPA and $^1O_2$, is a state selective process occurring from an upper excited singlet state of the endoperoxide (S_n, $n \geqslant 2$). Since the upper excited S_n state is short lived, the chemical deactivation pathway must be extremely efficient in order to compete with rapid radiationless relaxation to the lower energy states of the endoperoxide [19]. Indeed, the quantum yield to produce oxygen and the anthracene has a value of 0.28 [2] when the endoperoxide is directly excited to the upper π, π^* (S_n, $n \geqslant 2$) state, further attesting to the efficiency of the reaction. From our time-resolved measurements we know that the formation rate of the anthracene takes 95 ± 10 ps after direct excitation into the short-lived π, π^* state of the endoperoxide. In light of these facts we are forced to conclude that simultaneous formation of singlet oxygen and the ground state anthracene does not occur instantaneously, and thus does not follow a concerted mechanism as theoretically described by Kearns and Kahn [13–15].

We are left to consider two possible reaction pathways (scheme 3) that would be consistent with the observed kinetics of the delayed formation of the anthracene moiety. In one case there is a sequential C–O bond cleavage, which involves a 1,6-biradical intermediate. The two components of the 1,6-biradical intermediate are describable by a linked aromatic carbon radical and a peroxy radical. The decay of this biradical would be by recombination and/or by breaking the second C–O bond to produce $^1O_2$ and the ground state aromatic hydrocarbon.

The second case involves rapid expulsion of $^1O_2$ from the excited state endoperoxide leaving an excited valence anthracene isomer (which we describe as having a 1,4-aromatic biradicaloid structure). The excited valence isomer lifetime would then account for the slow formation time of the ground state anthracene. We differentiate this pathway from a concerted one of Kearns and Kahn [13–15] because the ground state anthracene is not produced simultaneously with $^1O_2$. We further point out that we also rule out a simple hemi-Dewar form [20–27] for the valence anthracene isomer, since the lifetimes (50–100 ps) that we observe are much shorter than the re-aromatization times found for ground state Dewar isomers, which are typically on the order of 10^{-6}–10^{-3} s [20–27].

The difference in the kinetics of 9,10-DPA-O_2 and 9,10-PA-O_2 is of particular interest. We find that the aromatic moiety is formed faster for 9,10-PA-O_2 compared to the diphenyl-substituted 9,10-DPA-O_2



Scheme 3. Biradical mechanism for upper excited state π, π^* state photofragmentation of aromatic endoperoxides. (A) Sequential C–O bond rupture to produce 1,6-biradical, or (B) fast rupture of both C–O bonds to produce $^1O_2$ and an excited anthracene valence isomer.

derivative. Such differences in the kinetics, due to the change in structure, was previously observed for the case of the isomers of the DMDPA-O_2 endoperoxide. The different kinetics in the derivatives may be resulting from changes in the stability of the short-lived intermediate produced in the reaction sequence. Evidence for this is based on the fact that the lifetime of the precursor π, π^* state is < 5 ps, and thus the rate determining step in the production of the aromatic moiety will be determined by the lifetime of the intermediate (scheme 2). At issue now is to determine whether there is a correlation between the molecular structure and the observed intermediate lifetimes.

If a biradical intermediate (either as the 1,6-peroxy-aromatic or as the 1,4-aromatic type) is involved in the pathway leading from S_2 to the final photoproducts, as proposed by us [11,16] and others [17,18], we can explain the observed kinetics in terms of how the molecular structure affects the biradical stability and thereby affect its lifetime. For instance, within the biradical model the lifetime of the intermediate decreases when there is either an increase in steric repulsions and/or decrease in resonance stabilization [28–30]. From table 1 we find that the longest lived intermediate is observed for the 9,10-DPA-O_2 derivative (95 ± 10 ps). We interprete this long lifetime as being a result of the stabilizing influence due to resonance interactions associated with the triphenyl methyl radical like center that would be produced following C–O bond cleavage (see table 2). A similar resonance effect should also be present for the 9,10-DMDPA-O_2 as well. However, a shorter intermediate lifetime of 75 ± 20 ps is found for the 9,10-DMDPA-O_2 derivative, which can be explained as resulting from the destabilizing influence of steric interactions between the methyl and phenyl groups in the biradical (see table 2). Thus, although the biradical intermediate produced from 9,10-DMDPA-O_2 should be stabilized by the strong resonance stabilization due to the triphenyl methyl like radical centers (as it would be for 9,10-DPA-O_2), the destabilizing influence due to steric interactions present means that it will be shorter lived.

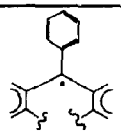
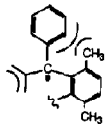
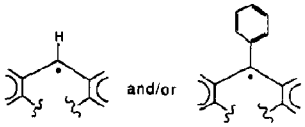
The effect of resonance interactions (or lack thereof) also explains the ordering of lifetimes observed for the other derivatives, as listed in table 1.

Table 1
Formation time of the ground state anthracene moiety following $S_0 \rightarrow S_n$ ($n \geq 2$) excitation, at 266 nm, of various endoperoxides in acetonitrile at ambient temperature

Endoperoxide [a]	Risetime (ps)
9,10-DPA-O_2	95 ± 10 [b]
9,10-DMDPA-O_2	75 ± 20 [c]
9,10-PA-O_2	60 ± 7 [b]
1,4-DMDPA-O_2	50 ± 15 [c]

[a] See text for structures. [b] This work. [c] ref. [11].

Table 2
Intermediate carbon radical centers derived from anthracene endoperoxide derivatives

Endoperoxide precursor	Carbon radical center
9,10-DPA-O_2	
9,10-DMDPA-O_2	
9,10-PA-O_2	
1,4-DMDPA-O_2	

For instance, the 60 ± 7 ps lifetime observed for the 9,10-PA-O_2 derivative is shorter than observed for the 9,10-diphenyl anthracene derivatives, i.e. 9,10-DPA-O_2 (95 ± 10 ps) or 9,10-DMDPA-O_2 (75 ± 20 ps). This result is consistent with the idea that for 9,10-PA-O_2 we would produce a diphenyl methyl like radical upon C–O cleavage at the C-10 position, whose stability is less than the triphenyl methyl radical like centers for the 9,10-diphenyl anthracene endoperoxide precursors.

Finally, when 1,4-DMDPA-O_2 undergoes C–O bond cleavage it will produce a biradical that lacks the enhanced resonance stabilization effects expected for the biradicals derived from either 9,10-DPA-O_2, 9,10-DMDPA-O_2 or 9,10-PA-O_2, i.e. it lacks the multiple phenyl groups being bonded directly to the carbon radical center. The short 50 ± 15 ps rise-time observed for the formation time of the aromatic moiety in 1,4-DMDPA-O_2 is consistent with this explanation.

3. Conclusions

Picosecond measurements show that excited state fragmentation of anthracene endoperoxides leading to the aromatic moiety and singlet oxygen is a multistep process involving a short-lived intermediate. The observation of the delayed appearance of the anthracene following photoexcitation into the upper π, π^* $S_n (n \geqslant 2)$ states as well as structural effects on the kinetics can be explained by an intermediate that is formed either by non-concerted, sequential C–O bond rupture, which involves a 1,6-biradical intermediate, or by the formation of an excited state anthracene valence isomer that has substantial biradical character.

Acknowledgement

We gratefully acknowledge the National Science Foundation, the Air Force Office of Scientific Research and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this work.

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