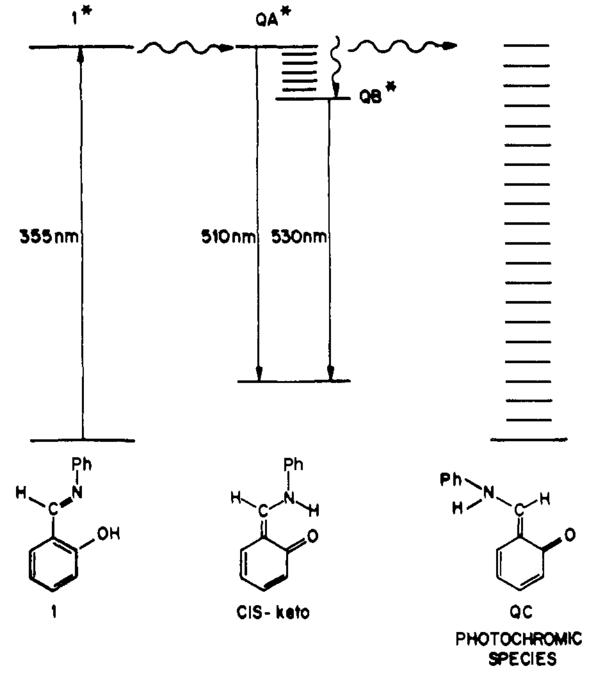
Scheme I. Simplified Schematic Representation of a Possible Photoisomerization Mechanism as Described in the Text[a]



[a] As discussed in ref 17, each of the labels 1, cis keto, and QP may actually represent several kinetically distinct conformers. QA* and QB* denote respectively vibrationally excited and vibrationally relaxed forms of the electronically excited "cis keto" molecule.

component of the fluorescence, which is blue shifted from the long-lived fluorescence, has tentatively been assigned to vibrationally excited fluorescence. This interpretation is consistent with the previously determined excitation wavelength dependence of the yield of fluorescence and photochromic species.[17] Several experiments are being planned to elucidate further the photochemical reaction mechanism. A systematic investigation of the bimodal fluorescence, as well as picosecond absorption studies, will be performed.

Our tentative assignment of vibrationally unrelaxed ("hot") fluorescence in such a large molecule is quite unusual and interesting. It may be that the "vibrational relaxation" we observe is torsional relaxation about the C_1–C_7 bond. Very little is known about internal vibrational redistribution, and/or vibrational and torsional energy transfer to the environment, in molecules of this size. Potentially, a thorough study of vibrationally excited fluorescence should lead to a better understanding of these phenomena. In reacting systems, these studies may lead to a better understanding of reactions driven by excess vibrational energy.

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(21) This observation shows that the cis keto isomer **Q1** does not have the same conformation as the excited cis keto isomer produced by excitation of the enol. As shown in reference 17, a large number of keto and enol conformations of **1** are actually possible.

Photolysis of the Endoperoxide of Heterocoerdianthrone. A Concerted, Adiabatic Cycloreversion Originating from an Upper Excited Singlet State

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Abstract: In the present work we report the photolysis of the endoperoxide (PO) of heterocoerdianthrone (HCD = dibenzo[*aj*]perylene-8,16-dione). Two different photoreactions were observed: (1) an irreversible decomposition of PO, whose reaction products were not analyzed (this reaction occurs with a quantum yield of $Q_{\text{dec}} = 0.006$ either from the $S_1(n,\pi^*)$ state or, more probably, from the $T_1(n,\pi^*)$ state); (2) a photoreversible cleavage of PO into HCD and O_2 (this reaction originates from the $S_2(\pi,\pi^*)$ state with a maximum quantum yield of $Q_1 = 0.26$). Only the very rapid internal conversion from $S_2(\pi,\pi^*)$ to $S_1(n,\pi^*)$ competes with this photoreaction. The products of the photocleavage are HCD in its ground state and O_2 in an electronically excited singlet state. These results confirm for the first time the predictions made by Kearns and Khan on the basis of state correlation diagrams concerning the concerted photocleavage of endoperoxides.

Introduction

In a recent article we introduced a new photochromic system which is based on the photoreversible addition of $O_2(^1\Delta_g)$ into an arene derivative.[1] The colored component is the red-violet heterocoerdianthrone (HCD = dibenzo[*aj*]perylene-8,16-dione). Self-sensitizing photooxidation of HCD leads to the formation of endoperoxide (PO), which in our photochromic

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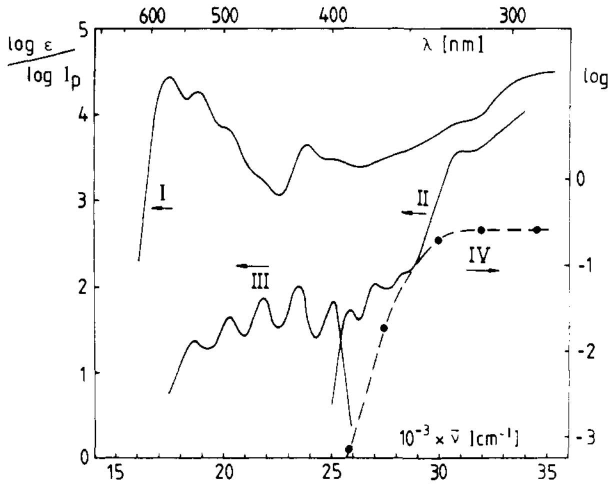
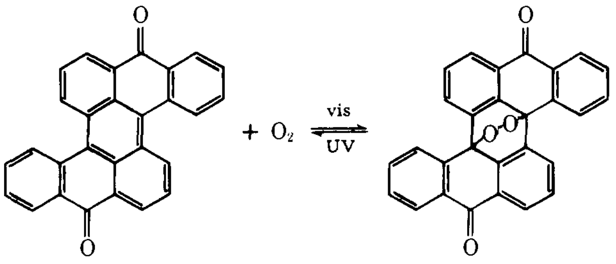


Figure 1. Absorption spectra of HCD (I) and PO (II) in toluene; corrected phosphorescence spectrum of anthrone (III) in MTH/toluene (1:1) at 96 K; the wavelength dependence of the quantum yield Q_1 for the photocleavage of PO into HCD and O_2 (IV) in aerated toluene whereby ● = experimental data. Error at 387.5 nm ±10%, at the other wavelengths ±4%. All representations are on a logarithmic scale.



HCD PO

system represents the colorless component. Upon UV irradiation of PO at 313 nm, the parent compounds HCD and O_2 are re-formed with a quantum yield of $Q_1 = 0.26$. During the photolysis of PO, decomposition products are also observed; however, the quantum yield for this irreversible side reaction is very small with $Q_{dec} = 0.004_5$ at 313 nm. Owing to the favorable ratio between both quantum yields, as well as the extraordinarily high thermal stability of both components, the new photochromic system has potential practical applications.

The photooxidation of HCD, as well as the thermolysis of PO, which once again produces the initial species HCD and O_2, is well studied and understood.[2-5] In contrast, the photolysis of PO has hardly been researched.

A number of questions remain unanswered, for example, whether the photolysis products HCD and O_2 are formed in their ground states or in their electronically excited states. Furthermore, the nature of the photoreactive state was, until now, unknown. The photolysis initial state could be either an excited singlet state or a triplet state. As the thermolysis of PO leads to the same products as photolysis, one cannot exclude the possibility that the reaction proceeds from an upper vibrational level of the ground state.

The fact that the quantum yield of photolysis was found to be much smaller than one seems to demonstrate the efficiency of the competing deactivation processes. However, it is also possible that electronically excited products are eventually formed (HCD in its ground state and $O_2(^1\Delta_g)$ or HCD in its first exited singlet state and O_2 in its ground state) and recombine while still in the solvent cage. This would also result in a lower quantum yield of photolysis. In order to answer these questions we have examined the photolysis of PO in detail and report our findings in the following text.

Experimental Section

Dibenzo[*aj*]perylene-8,16-dione (HCD) was prepared and purified as previously described,[1,6] fp 634 K.

2,10-Dibromodibenzo[*aj*]perylene-8,16-dione (DBHCD) was made from anthraquinone-1,5-dicarboxylic acid dichloride and bromobenzene analogously to the known synthesis of 2,10-dichlorodibenzo[*aj*]perylene-8,16-dione.[6] Purification was accomplished by repeated recrystallization from pyridine and xylene. Red-violet crystals of fp >673 K were obtained. Anal. Calcd for $C_{28}H_{12}O_2Br_2$: C, 62.2; H, 2.2; Br, 29.6. Found: C, 61.7; H, 2.5; Br, 28.3.

The absorption spectra of DBHCD and HCD (see Figure 1) are identical.

The preparation and purification of endoperoxide PO are described in a preliminary work.[1] Tetramethyl-1,2-dioxetane was synthesized and purified according to known methods in the literature.[7] 1,3-Diphenylisobenzofuran (EGA) and 9,10-dibromoanthracene (Aldrich-Europe) were purified by repeated recrystallization from ethanol. Anthrone (Merck-Schuchardt) was recrystallized from benzene. Toluene (Merck Uvasol, spectroscopic grade) and dibromomethane (Fluka, puriss.) were used without further purification. Benzyl alcohol (Fluka) and xylene (Merck) were carefully purified by vacuum distillation. 2,3-Dimethyl-2-butene from EGA was used without further purification.

Absorption spectra were recorded on a Zeiss DMR 10 spectrophotometer. The apparati for the determination of the photochemical quantum yields and for the fluorescence measurements are described in detail in an earlier work.[4] GC analysis was performed on a Perkin-Elmer PE 900 HF gas chromatograph.

Nearly all experiments were run at room temperature. Only the intensities of the indirect chemiluminescence were determined at 313.2 ± 0.1 K. These measurements were performed in a manner described elsewhere.[8]

Results and Discussion

1. The Initial State of Photocleavage. The absorption spectra of HCD and PO are illustrated in Figure 1. The low-energy absorption band of PO reaches its first maximum at 28 500 cm^{-1}. This band shows vibrational structure and has a low extinction coefficient: ϵ_{25800} 52 M^{-1} cm^{-1}. We assign it to the $S_0 \rightarrow S_1(n,\pi^*)$ transition of the carbonyl group. The second band, whose low-energy shoulder lies at 30 700 cm^{-1}, has a significantly higher extinction coefficient: ϵ_{30700} 3550 M^{-1} cm^{-1}. This band is assigned to the $S_0 \rightarrow S_2(\pi,\pi^*)$ transition.

Generally, the π^*,σ^* transition for dialkyl-substituted peroxides is assigned to the broad band at approximately 29 000-50 000 cm^{-1}, which has a maximum extinction coefficient of only $\epsilon \approx 10$ M^{-1} cm^{-1}.[9] As the peroxide bridge in PO also connects sp^3-hybridized carbon atoms, a marked red shift of this absorption in comparison to dialkyl peroxides is not expected. Owing to the low oscillator strength and the position of the absorption in the range of the π,π^* band, an additional absorption band of the peroxide chromophore in the spectrum of PO could not be observed. Therefore it is impossible to decide whether the π,π^* band still corresponds to the transition $S_0 \rightarrow S_2$ as proposed, or already to the transition $S_0 \rightarrow S_3$.

Fluorescence emission from PO could be observed by irradiating neither the $S_1(n,\pi^*)$ nor the $S_2(\pi,\pi^*)$ band.

The position and character of the T_1 state (n,π^* or π,π^*) could not be determined, because no phosphorescence emission of PO was observed, even at 96 K in a degassed, rigid solution (methyltetrahydrofuran/toluene, 1:1). In contrast, the phosphorescence emission of anthrone, which was investigated for the purpose of comparison, could be detected under identical conditions. This compound has a similar absorption spectrum

anthrone

to that of PO[1,10] ($S_1(n,\pi^*)$ at 26 600 cm^{-1}, $S_2(\pi,\pi^*)$ at 34 200 cm^{-1}) because of their related electronic structures. The strongly structured phosphorescence spectrum is also depicted in Figure 1. The energetically highest vibrational band lies at 25 100 cm^{-1} and the vibrational progression amounts to 1600 cm^{-1}. In accordance with the results of other authors,[10] the T_1 state of anthrone is found at 25 100 cm^{-1} and possesses n,π^* character.

No fluorescence emission was observed for anthrone, as was also the case for PO. This is due to the extraordinarily rapid intersystem crossing (isc) from $S_1(n,\pi^*)$ to $T_1(n,\pi^*)$, which according to Kobayashi and Nagakura is complete within 70 ps,[10] although recent measurements by Damschen et al. indicate that isc occurs in only 10 ps.[11]

On the basis of the similarity in the absorption spectra of PO and anthrone, the position and character of the lowest singlet states are nearly identical. If this analogy can be transferred to the triplet states, as well as to isc, then the T_1 state of PO should possess $n\pi^*$ character and can be localized at ca. 24 300 cm^{-1}. Moreover, the extremely rapid isc of $S_1(n,\pi^*)$ to $T_1(n,\pi^*)$ would then inhibit the fluorescence emission, as is the case in anthrone. Why no phosphorescence of PO was observed remains unanswered.

In order to eludicate the nature of the initial state of the photolysis of PO, we investigated the quantum yield Q_1 for the formation of HCD as a function of wavelength. This was accomplished by monitoring spectrophotometrically the production of HCD at its absorption maximum at 573 nm. Owing to the fact that the product HCD absorbs at the irradiation wavelengths (see Figure 1), the photolysis was terminated after 1-5% conversion and, where necessary, corrected for the absorption by HCD. The observed wavelength dependence of Q_1 is also illustrated in Figure 1. At $\lambda < 334$ nm Q_1 approaches a limit and at 313 and 290 nm has a value of $Q_1 = 0.26 \pm 0.01$. For $\lambda > 334$ nm Q_1 decreases sharply such that at the low-energy maximum of the PO absorption Q_1 is only $(7 \pm 0.7) \times 10^{-4}$ at 387.5 nm.

This result establishes that the $S_1(n,\pi^*)$ state of PO cannot be the initial state for the photochemical cleavage into HCD and O_2. The very small value found for Q_1 by irradiating the $S_1(n,\pi^*)$ band might be due to stray light passing through the irradiation monochromator, but more probably results from an overlapping absorption of the $S_2(\pi,\pi^*)$ band at 387.5 nm.

Furthermore, the possibility of a reaction from upper vibrational levels of the S_0 ground state can also be discounted on the basis of the observed wavelength dependence of Q_1. Internal conversion into these levels from $S_1(n,\pi^*)$ should be more likely than from $S_2(\pi,\pi^*)$, because of the smaller energy gap to S_0 and the probable not shorter lifetime of $S_1(n,\pi^*)$ relative to $S_2(\pi,\pi^*)$. The drastic decrease in Q_1 which results when the $S_1(n,\pi^*)$ band is irradiated instead of the $S_2(\pi,\pi^*)$ band cannot therefore be rationalized with a reaction in the electronic ground state.

As mentioned above, a rapid deactivation of the S_1 state of PO by isc to the T_1 state is probable because of the similarity of the electronic structures of anthrone and PO. Therefore, it is unlikely that photocleavage originates from the T_1 state.

The validity of this reasoning can be tested by conducting sensitized photolysis experiments. In these experiments we used the sensitizer T_1 acetone, which is produced selectively and in a high yield during the thermolysis of tetramethyl-1,2-dioxetane (TMD).[12,13] The T_1 state of the donor acetone has sufficient energy (27 300 cm^{-1}) to allow an exothermic and spin-allowed energy transfer to the T_1 state of PO to occur. In this case triplet-triplet energy transfer should be diffusion controlled, which means that the rate constant of TT energy transfer in toluene at 313 K is expected to be $k_{\mathrm{ET}}{}^{\mathrm{TT}} \approx 10^{10}$ M^{-1} s^{-1}.[14]

Excitation of the S_2 state of PO by energy transfer from T_1 acetone can thereby be excluded, as this state lies about 3400 cm^{-1} above the T_1 state of the donor. Excitation of the S_1 state, which lies below the T_1 state of the donor, can also be eliminated. This is due to the fact that exothermic triplet-singlet energy transfer from T_1 acetone to acceptors such as anthracene, which have no internal heavy-atom effect, is observed only with rate constants of $k_{\mathrm{ET}}{}^{\mathrm{TS}} \approx 2 \times 10^6$ M^{-1} s^{-1} in toluene.[8,15]

In order to examine the hypothesis that TT energy transfer to PO takes place, we measured the intensities of chemiluminescence I_0 and I of solutions of TMD and 9,10-dibromoanthracene (DBA) and of TMD, DBA, and PO, respectively, in toluene at 313.2 K. Equations 1 and 2 hold for the intensities I_0 and I:

$$I_0 = K[\mathrm{TMD}]k_{\mathrm{ET}}[\mathrm{DBA}]/(k_{\mathrm{ET}}[\mathrm{DBA}] + k_{\mathrm{DEA}}{}^{\mathrm{TA}}) \quad (1)$$

$$I = K[\mathrm{TMD}]k_{\mathrm{ET}}[\mathrm{DBA}]/(k_{\mathrm{ET}}[\mathrm{DBA}] + k_{\mathrm{DEA}}{}^{\mathrm{TA}} + k_{\mathrm{X}}[\mathrm{PO}]) \quad (2)$$

[TMD], [DBA], and [PO] represent the actual concentrations of the luminescent solutions; K is a constant. k_{ET} and k_{X} are the rate constants of energy transfer to DBA and to PO and $k_{\mathrm{DEA}}{}^{\mathrm{TA}}$ is the rate constant of deactivation of T_1 acetone in toluene.

Using the already published constants $k_{\mathrm{ET}} = 2.6 \times 10^{10}$ M^{-1} s^{-1} and $k_{\mathrm{DEA}}{}^{\mathrm{TA}} = 5 \times 10^7$ s^{-1},[15] and the concentrations [TMD] = 3.0×10^{-3} M, [DBA] = 1.65×10^{-4} M and [TMD] = 2.0×10^{-3} M, [DBA] = 1.1×10^{-4} M, and [PO] = 1.1×10^{-3} M, respectively, and the observed ratio of $I_0/I = 2.70$, one obtains $k_{\mathrm{X}} = 1.1 \times 10^{10}$ M^{-1} s^{-1}. This result demonstrates that T_1 acetone excites the T_1 state of PO by TT energy transfer.

If the T_1 state of PO is the initial state of photocleavage, then one should observe during the thermolysis of TMD in the presence of PO and in the absence of light the production of HCD. For concentrations of [TMD] = 5×10^{-3} M and [PO] = 2×10^{-3} M and a thermolysis time of $\Delta t = 8400$ s at 313.2 K, the spectrophotometrically determined increase in [HCD] amounted to $\Delta[\mathrm{HCD}] = 1.4 \times 10^{-7}$ M. This increase is ca. five times larger than the HCD production which only results from the slow thermolysis of PO.[5]

TMD decays at 313.2 K with a rate constant of $k_{\mathrm{T}} = 7.64 \times 10^{-6}$ s^{-1},[16] whereby T_1 acetone is produced with a yield of $\Phi^{\mathrm{T}} = 0.3$.[13] As [TMD] decreases in 8400 s only by about 6%, eq 3 approximately describes the minimum production of HCD, provided that the photocleavage originates from the T_1 state of PO and the reaction probability lies in the range of 0.26 (the maximum value for Q_1) and 1.

$$\Delta[\mathrm{HCD}] = k_{\mathrm{T}}[\mathrm{TMD}]\Delta t\Phi^{\mathrm{T}}(0.26)k_{\mathrm{X}}[\mathrm{PO}]/(k_{\mathrm{X}}[\mathrm{PO}] + k_{\mathrm{DEA}}{}^{\mathrm{TA}}) \quad (3)$$

With the given values one calculates from (3) $\Delta[\mathrm{HCD}] = 7.7 \times 10^{-6}$ M. This result exceeds the experimentally determined result by a factor of 50.

Hence it follows that the T_1 state of PO cannot be the initial state of the photocleavage into HCD and O_2. The slight increase in [HCD] is indeed caused by sensitized photolysis of PO, but in this case S_1 acetone, which is produced in a very small yield during the thermolysis of TMD, acts as the donor. S_1 acetone may then excite the S_2 state of PO by singlet-singlet energy transfer.

From our investigations it follows that the T_1 state and the S_1 state, as well as the upper vibrational levels of the S_0 state, can be excluded as initial states of the photocleavage. The results are consistent with the assumption that this reaction originates from the S_2 state. As one finds the same value at 290 nm for Q_1 as at 313 nm, the photoreactive state is the thermally equilibrated S_2 state.

Table I. Concentration Changes of HCD and DPI during the Trapping Experiment[a]

t, min	10^5[HCD], M	10^5[DPI], M
0	0.19	4.59
5	0.42	4.34
10	0.61	4.23
15	0.84	4.11
20	1.07	4.00
25	1.32	3.92
30	1.55	3.81
35	1.73	3.71
40	1.96	3.62

[a] λ 313 nm, $I_{abs} = 8.4 \times 10^{-9}$ einstein min^{-1}, $V = 0.0037$ L.

2. The Photolysis Products. By irradiation of the $S_2(\pi,\pi^*)$ band mainly HCD and O_2 are regenerated. The irreversible formation of byproducts can only be observed to a small extent. The ratio of the quantum yields of HCD formation to the formation of byproducts is $Q_1/Q_{dec} \approx 60$ at 313 nm.[1]

It is of particular interest to determine whether the photolysis products, HCD and O_2, are formed primarily in their electronically excited states. According to a theory of Kearns and Khan, the O_2 formed by photochemically induced cycloreversion of endoperoxides is predicted to be in its electronically excited $^1\Sigma_g{}^+$ state, while the parent hydrocarbon should be generated in its ground state.[17-19]

The photolysis of nearly all endoperoxides investigated up to now results in the formation of rearranged products.[20] An exception is the endoperoxide of 9,10-diphenylanthracene, the photolysis of which leads to the partial regeneration of the parent compound, as established by Rigaudy et al.[21] PO is the first endoperoxide whose photolysis results in the near-quantitative formation of the educts of photooxidation, i.e., the hydrocarbon and oxygen. Therefore it should now be possible to test the predictions of Kearns and Khan by experimental investigations.

For this reason we have tried to identify electronically excited products by luminescence measurements and experiments with singlet oxygen traps.

1,3-Diphenylisobenzofuran (DPI) reacts very rapidly with $O_2(^1\Delta_g)$ ($k = 7 \times 10^8$ M^{-1} s^{-1})[22] and is therefore especially suitable as a singlet oxygen trap.[23]

If the photolysis of PO is performed at 313 nm in the presence of DPI, the latter will always absorb part of the irradiated light. Owing to the fact that DPI undergoes a self-sensitized reaction with oxygen, it can only be a useful singlet oxygen trap when the solutions are most carefully degassed. In this case only the oxygen produced by photolysis of PO is available for the self-sensitized photooxidation of DPI. If moderate light intensities are used for photolysis of a small fraction of the PO and the solutions are stirred, then the evolved oxygen has sufficient time to diffuse into the gas phase and the O_2 concentration in the solution remains so small that the self-sensitized photooxidation of DPI can be neglected.

A toluene solution of [PO] = 4.25×10^{-4} M and [DPI] = 4.59×10^{-5} M was degassed by six thaw and freeze cycles at 1.8×10^{-8} bar. The magnetically stirred solution was then irradiated in a sealed 1-cm cuvette at 313 nm. An absorption spectrum was recorded every 5 min, whereby the formation of HCD and the disappearance of DPI could be followed at the absorption maxima at 573 and 417 nm, respectively. The total irradiated light intensity of 8.4×10^{-9} einstein min^{-1} was absorbed. Initially, the fraction of light absorbed by PO was 80% and that by DPI 20%.

A solution of DPI in toluene in the absence of PO was prepared in the same way and showed no change in concentration after 45-min irradiation with a fivefold light intensity. Therefore, it can be concluded that the observed decrease in the DPI concentration during the trapping experiment results predominantly from the reaction of DPI with the $O_2(^1\Delta_g)$ generated in the photolysis of PO.

The concentration vs. time data obtained from the trapping experiment are given in Table I. The HCD formed during photolysis reacts far slower with $O_2(^1\Delta_g)$ than DPI.[4] Therefore, in the investigated concentration range $O_2(^1\Delta_g)$ is only consumed by reaction with DPI and by physical deactivation with the rate constant k_{dea}. HCD and O_2 are generated in equimolar proportions. Using the photostationary state approximation, one obtains

$$(\alpha)\mathrm{d[HCD]}/\mathrm{d}t = (k_{dea} + k\mathrm{[DPI]})[^1O_2] \qquad (4)$$

where α is the yield of $^1O_2$ with respect to the total amount of evolved oxygen.

The reaction of DPI follows a second-order rate law:

$$-\mathrm{d[DPI]}/\mathrm{d}t = k\mathrm{[DPI]}[^1O_2] \qquad (5)$$

From eq 5 one can approximate the photostationary concentration of $^1O_2$:

$$[^1O_2] \approx -\mathrm{d}\ln\mathrm{[DPI]}/\mathrm{d}t(k) \qquad (6)$$

Combination of eq 4 and 6 results in

$$\alpha \approx -\frac{\mathrm{d}\ln\mathrm{[DPI]}}{\mathrm{d[HCD]}}(\beta + \overline{\mathrm{[DPI]}}) \qquad (7)$$

where $\overline{\mathrm{[DPI]}}$ represents the mean concentration of DPI throughout the duration of the experiment and $\beta = k_{dea}/k$. A plot of ln [DPI] vs. [HCD] shows the linear correlation expected from eq 7 with a slope of d ln [DPI]/d[HCD] = 11 400 M^{-1}. Taking the known values of $\overline{\mathrm{[DPI]}} = 4.1 \times 10^{-5}$ M and $\beta = 5 \times 10^4/7 \times 10^8 = 7 \times 10^{-5}$ M,[22] an $^1O_2$ yield emerges of $\alpha \approx 1.2_7 \pm 0.4$.

The source of errors in α can be traced to the uncertainties in β as well as to the concentration measurements.

Owing to the importance of $^1O_2$ formation in the classification of the photolysis as an adiabatic reaction both referees stressed the need to verify its existence during photolysis by a second independent method.

On the basis of a suggestion of one of the referees, photolysis of PO was conducted in the presence of 2,3-dimethyl-2-butene (DMB) as a singlet oxygen trap. While the production of HCD could be followed spectrophotometrically, the formation of the oxidation product of DMB was measured by GC. As a result of these measurements, the oxidation product was characterized as 3-hydroxy-2,3-dimethyl-1-butene (HDMB).[24] An important advantage of this method is that by irradiating at 313 nm the $^1O_2$ acceptor does not absorb.

In our experiments, a degassed toluene solution of [DMB] = 0.17 M and [PO] = 2.03×10^{-3} M was photolyzed under N_2. As HCD reacts not much faster with $^1O_2$ than DMB and as the β value of DMB (10^{-3} M) is more than two orders of magnitude smaller than that of [DMB], the evolved $^1O_2$ is completely trapped by DMB.

Therefore, in this concentration range, it follows that

$$\alpha = \mathrm{d[HDMB]/d[HCD]}$$

In other words, α is no longer dependent on the relatively unsure β value.

At certain time intervals, the irradiation was interrupted and the concentrations of HCD and HDMB were determined. The obtained values are shown in Figure 2. A linear relationship was obtained, where only the first [HDMB] value deviates. The slope of the line amounts to $\alpha = 1.0 \pm 0.1$, whereby the error in α is mainly due to the error in the HDMB concentration determinations.

This clearly establishes that O_2 is formed with a unit yield in an electronically excited singlet state during the photolysis of PO. Though it was trapped as $O_2(^1\Delta_g)$, it may have been primarily generated as $O_2(^1\Sigma_g{}^+)$.

Similarly, the photolysis product HCD could also have been originally formed in an excited singlet state. In this case, the fluorescence emission of HCD should be observed from the beginning of the photolysis of pure PO solutions. Owing to the fact that the photolysis product HCD absorbs some of the irradiated light, an additional increase of the fluorescence emission of HCD will always be observed. By comparison of the HCD fluorescence of solutions containing only PO or pure HCD, an estimation can be made of the extent to which HCD is formed in its S_1 state during PO photolysis.

The luminescence intensity I_1 of the pure PO solution can be expressed as

$$I_1 = AI_{abs}(\mathrm{PO})Q_1\gamma Q_f \qquad (8)$$

with A an apparatus constant, $I_{abs}(\mathrm{PO})$ the fraction of light absorbed by PO, Q_f the fluorescence quantum yield of HCD, and γ the yield of HCD in its S_1 state with respect to the total amount of the generated HCD.

The luminescence intensity I_f of a HCD solution, under the same conditions, obeys the equation

$$I_f = AI_{abs}(\mathrm{HCD})Q_f \qquad (9)$$

If the optical densities D of both solutions at the irradiation wavelength of 313 nm are equal, one can derive

$$\gamma = I_1/I_fQ_1 \qquad (10)$$

For $D = 1.21$ of the PO and HCD solutions we obtained

$$\gamma = 0.1/(50 \times 0.26) \approx 8 \times 10^{-3}$$

Within the limits of uncertainty one can say that no HCD is formed in its excited singlet state during the photolysis of PO.

3. Competing Deactivation Processes. The quantum yield Q_1 is found to be fairly small, even when the reactive $S_2(\pi,\pi^*)$ state is excited. Obviously there exist deactivation processes which compete efficiently with the photocleavage.

However, there may also exist a chemical process which reduces the quantum yield; e.g., the products HCD and $O_2(^1\Delta_g)$ may recombine to form PO in the initial solvent cage. This is possible because the lifetime of $O_2(^1\Delta_g)$ is much longer than that of the cage.[4,25] The probability of reaction can then be enhanced by reencounter. The diffusion of the geminate photocleavage products out of the initial solvent cage competes with recombination. Thereby the rate of diffusion should be, in a first approximation, inversely proportional to the viscosity η of the solvent.

In order to test whether Q_1 is a function of η, we not only determined Q_1 in toluene, but also in benzyl alcohol. The reaction conditions were identical and irradiation was conducted at 313 nm. Although the viscosity of benzyl alcohol ($\eta = 5.8 \times 10^{-3}$ Pa·s) at 293 K is ten times larger than that of toluene ($\eta = 5.9 \times 10^{-4}$ Pa·s), we found a value for Q_1 of 0.18, which is only about 30% smaller than in toluene. where Q_1 equals 0.26.

This result shows that the recombination of the photocleavage products in the initial solvent cage does not play an important role. Apparently the reactivity of the photolytically created $^1O_2$ with HCD is similar to that of $O_2(^1\Delta_g)$, which is produced during the photooxidation of HCD by energy transfer. In the case of photooxidation, the reaction probability p of a geminate HCD-$O_2(^1\Delta_g)$ pair in a common solvent cage was determined to be $p = 0.015$.[4]

Possible physical deactivation processes. which can compete with the photocleavage, are isc from $S_2(\pi,\pi^*)$ into the triplet state system or internal conversion (ic) from $S_2(\pi,\pi^*)$ to $S_1(n,\pi^*)$. In the case where isc is an effective competing process. the quantum yield of photocleavage should depend on the heavy-atom effect.

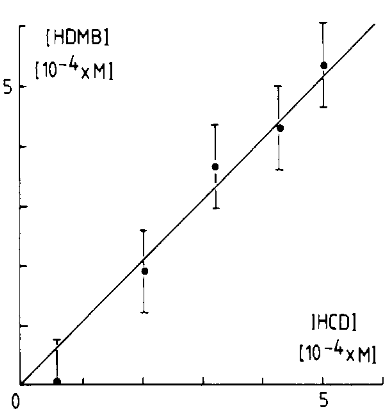


Figure 2. Plot of the increase in [HDMB] against the increase in [HCD] during the photolysis of PO (λ_{irr} 313 nm).

Table II. Q_1 as a Function of $[CH_2Br_2]$, λ 334 nm

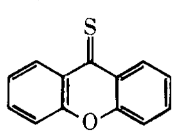
$[CH_2Br_2]$, M	0	0.208	0.406	0.775
Q_1	0.20_3	0.20_1	0.20_6	0.21_0

In order to determine the external heavy-atom effect we investigated Q_1 as a function of $[CH_2Br_2]$ at 334 nm in toluene. The values which are given in Table II demonstrate that an external heavy-atom effect does not exist.

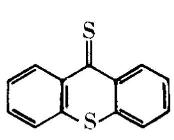
The influence of the inner heavy-atom effect on the photocleavage was examined by measuring Q_1 of a solution of the endoperoxide of DBHCD. For that purpose a solution of the dibromo derivative of HCD was first completely photooxidized and then photolyzed at 313 nm in the usual manner. We determined the same value for Q_1 of 0.26 as was found for PO.

Therefore, no influence of an inner or an external heavy-atom effect on the photocleavage of PO could be detected. Apparently only ic from the $S_2(\pi,\pi^*)$ state to the $S_1(n,\pi^*)$ state competes with the reversible photoreaction.

The energy gap between S_2 and S_1 amounts to $\Delta E_{SS} = 4900$ cm^{-1} and is smaller than in the case of xanthione ($\Delta E_{SS} = 7500$ cm^{-1}) or thioxanthione ($\Delta E_{SS} = 6800$ cm^{-1}).[26,27] For these two compounds, which have an electronic structure similar to that of PO, fluorescence $S_2 \rightarrow S_0$ and photochemical reactions occurring from the S_2 state could be observed.[28] The prerequisite for these processes is the observed relatively long lifetime of the $S_2(\pi,\pi^*)$ state, which is also mainly limited by ic to $S_1(n,\pi^*)$ as was found for PO. From measurements of the fluorescence quantum yields, the rate constants of ic were calculated for xanthione to be $k_{ic} = 2.1 \times 10^{10}$ s^{-1} and for thioxanthione to be $k_{ic} = 3.4 \times 10^{10}$ s^{-1}.[26] On the other hand, Anderson and Hochstrasser estimated a value of $k_{ic} = 8 \times 10^{10}$ s^{-1} for xanthione from direct measurements of the S_2 lifetime.[29] On the basis of the energy-gap law, one can assume that for PO ic from S_2 to S_1 is even more rapid, such that k_{ic} may be placed in the range of $k_{ic} \approx 10^{11}$-10^{12} s^{-1}. As one can observe photocleavage despite the rapid deactivation of the S_2 state, the photoreaction must then occur in a time range of 10^{-11}-10^{-12} s.



xanthione



thioxanthione

4. The Side Reaction. By irradiating the photochemical equilibrium at λ 313 nm one observes a slight decrease in [HCD] resulting from an irreversible photochemical side reaction. With the assumption that this side reaction occurs by irradiating PO and not HCD. one calculates the quantum yield to be $Q_{dec} = 0.004_5 \pm 0.001$.[1]

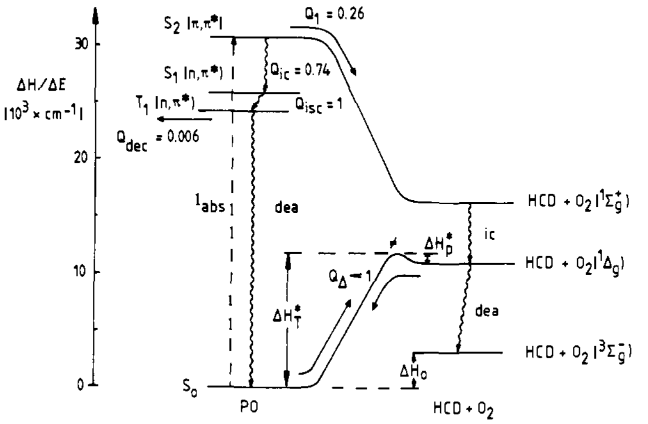


Figure 3. Reaction scheme of the photoreversible and photochromic system

$$\mathrm{HCD} + \mathrm{O_2} \underset{\mathrm{UV}/\Delta}{\overset{\mathrm{vis}}{\rightleftarrows}} \mathrm{PO}$$

Q_Δ is the yield of $O_2(^1\Delta_g)$ during the thermolysis of PO; for description, see text.

During the irradiation of the $S_1(n,\pi^*)$ band with λ 387.5 nm one can observe, in addition to the small production of HCD ($Q_1 = 0.0007$), the formation of one or several byproducts, whose low-energy absorption bands lie at about 420 nm. Although these byproducts were not analyzed, an attempt was made to determine the quantum yield $Q_{\mathrm{dec}}(n,\pi^*)$ of this process. For that purpose it was necessary to estimate the decrease in [PO], the increase in [HCD], and the light intensity absorbed by PO.

A solution (2.5 cm³) of [PO] = 1.23×10^{-3} M in xylene was irradiated with an intensity of $I_0 = 1.2 \times 10^{-7}$ einstein/min at 387.5 nm for 4402 min. Initially the optical density was $D^b = 0.064$ in a 1-cm cuvette at the irradiation wavelength. Owing to the formation of side products and HCD, the optical density of the solution increased to $D^e = 0.185$ at the end of irradiation.

The slight increase in [HCD] could be determined spectrophotometrically at the maximum at 573 nm to be 1.7×10^{-5} M. In order to estimate the decrease in [PO], the irradiated and a nonirradiated solution were heated for 100 min to 413 K in the dark. By this procedure the remaining PO thermolyzes completely to HCD. By comparison of the HCD absorption of both samples, we determined the unphotolyzed fraction of PO to be 87%. Therefore the total decrease in [PO] amounted to $0.13 \times 1.23 \times 10^{-3} = 1.6 \times 10^{-4}$ M, from which 1.7×10^{-5} M was converted by photocleavage to HCD and O_2 and 1.43×10^{-4} M was decomposed by the side reaction.

The fraction of the total optical density attributable to PO was $0.87 \times 0.064 = 0.056$ at the end of irradiation.

The absorbed light intensity I_{abs} can be calculated by

$$I_{\mathrm{abs}} = (1 - 10^{-D})I_0(1 - R) \qquad (11)$$

with $R = 0.04$ being the loss due to reflection at the surface of the cuvette. At the beginning the absorbed light intensity was $I^b_{\mathrm{abs}} = 0.132 I_0$, while at the end $I^e_{\mathrm{abs}} = 0.333 I_0$. However, at the end only the fraction $0.333 I_0(0.056/0.185) = 0.101 I_0$ was absorbed by PO. Therefore, the light intensity, which is absorbed by PO, decreases slightly during photolysis. If one assumes a mean constant absorbed light intensity of $0.116 I_0$, then one can calculate

$$Q_{\mathrm{dec}}(n,\pi^*) = \frac{1.43 \times 10^{-4} \times 0.0025}{0.116 \times 1.2 \times 10^{-7} \times 4402}$$

$$Q_{\mathrm{dec}}(n,\pi^*) = 0.0058$$

By irradiating the $S_2(\pi,\pi^*)$ band at λ 313 nm, photocleavage of PO occurs with $Q_1 = 0.26$. As internal conversion is the only competing process, the $S_1(n,\pi^*)$ state will be reached with a yield of 0.74. The side reaction then takes place with $Q_{\mathrm{dec}}(n,\pi^*) = 0.0058$. Consequently, the quantum yield of the side reaction at 313 nm, $Q_{\mathrm{dec}}(\pi,\pi^*)$, should amount to $Q_{\mathrm{dec}}(\pi,\pi^*) = 0.74 \times 0.0058 = 0.0043$. This result is in good agreement with the value of 0.004_5, which was determined by irradiation of the photochemical equilibrium.

The lifetime of the $S_1(n,\pi^*)$ state of PO is presumably completely limited by a rapid isc into the triplet system. As in the case of anthrone, the lifetime may be in the range of 10^{-11} to 5×10^{-11} s. Therefore, it is more probable that, after isc has occurred, the side reaction starts from the longer lived $T_1(n,\pi^*)$. The side reaction could involve H abstraction from the solvent, which is a commonly accepted reaction for triplet states of aromatic ketones.

5. Comparison of the Experimental Results with Theoretical Predictions. Several years ago, Kearns and Khan[17,18] derived selection rules for the concerted addition of O_2 onto cis dienes. Based on orbital and state correlation diagrams, predictions were made concerning the nature of the products and product states resulting from the thermolysis and photolysis of endoperoxides. As a result, the thermolysis of endoperoxides could be anticipated to yield $O_2(^1\Delta_g)$.[17-19] Indeed, this was verified initially by Wassermann et al. and later, quantitatively, by Turro et al.[23,30,31]

Furthermore, the theory of Kearns and Khan leads to the conclusion that the diradical fragmentation of the O-O bond should compete with the concerted loss of molecular oxygen during the photolysis of endoperoxides of dienes. Moreover, the diradical fragmentation, which results in the formation of rearranged products, should occur from the S_1 and T_1 states. Liberation of O_2 from these states is unlikely because of the existence of energy barriers.

However, by irradiation of a higher singlet state a concerted dissociation of peroxides into $O_2(^1\Sigma_g{}^+)$ and the parent diene is predicted to take place.

Following the hypothesis of Kearns and Khan, these predictions are also valid for the photochemical behavior of the endoperoxides of aromatic hydrocarbons. An analogous treatment of the photolysis of PO can be realized if one takes into account that the lowest excited singlet and triplet states of PO are of n,π^* character instead of π^*,σ^* character. This modification will probably alter the nature of the photochemical reaction from S_1 and T_1—most likely involving H abstraction instead of breaking of the peroxide bridge—but the priority of the photochemical reactions should not be affected.

In actual fact, the photochemical decomposition of PO into HCD and O_2 occurs exclusively from the $S_2(\pi,\pi^*)$ state and not from the S_1 or T_1 states. In agreement with the above theory, O_2 is formed in an excited singlet state. The fact that O_2 is trapped as $O_2(^1\Delta_g)$ may well be due to the very short lifetime of primary formed $O_2(^1\Sigma_g{}^+)$ in solution as $O_2(^1\Sigma_g{}^+)$ is deactivated to $O_2(^1\Delta_g)$ within about 10^{-12} s.[32] The extraordinarily short reaction time of 10^{-11}–10^{-12} s estimated for the photocleavage is also in agreement with an adiabatic process.

The agreement between the theoretical and experimental results leads to the conclusion that the photocleavage of PO into HCD and $^1O_2$ is a concerted, adiabatic cycloreversion.

It remains unclear why the photolysis of nearly all the endoperoxides investigated up to now—including those derived from aromatic hydrocarbons—was not observed to yield O_2 and the hydrocarbon.[20,33] This reaction path may be discovered to exist more often when careful investigations of the photochemistry of endoperoxides are made. On the other hand, PO may prove to be an exception.

From further systematic studies of the photochemistry of endoperoxides, we intend to clarify whether these processes are not only controlled by simple selection rules, but also by other factors.

6. Summary. In Figure 3 the results of the photolysis and thermolysis[5] of PO, as well as the photooxidation[4] of HCD, are compiled in one diagram. Here the reaction paths of the photoreversible and photochromic system

$$\mathrm{HCD} + \mathrm{O_2} \underset{\mathrm{UV}/\Delta}{\overset{\mathrm{vis}}{\rightleftharpoons}} \mathrm{PO}$$

are reported. The construction of this scheme thereby follows the state correlation diagram envisaged by Kearns and Khan.[17-19] The state diagrams of PO and the pair, HCD-O_2, are depicted on a linear scale on the left- and right-hand sides of Figure 3, respectively. The observed reactions are characterized by continuous arrows. Initial and product states are connected by full lines. The enthalpies of activation of thermolysis and of photooxidation, $\Delta H_T^{\ddagger}$ and $\Delta H_P^{\ddagger}$, are given, as well as the difference in enthalpies between HCD and PO, ΔH_0. The wavelike arrows represent radiationless deactivation processes and the dashed arrow the absorption process.

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Thermal Isomerization of Allyl-Substituted Cyclopropenes. An Example of a Nonsynchronous Cope Rearrangement

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Abstract: The thermal Cope rearrangement of a number of allyl-substituted cyclopropenes has been studied in mechanistic detail. Thermolysis of 1,2-diphenyl-3-allyl-3-methylcyclopropene produced an equilibrium mixture of recovered starting material (35%), 1,3-diphenyl-2-methyl-3-allylcyclopropene (13%), and 1,2-diphenyl-6-methyltricyclo[2.2.0.$0^{2,6}$]hexane (52%). The rates and corresponding Arrhenius parameters were determined and compared to model systems. The thermal chemistry of the closely related 3-(1-methylallyl)-substituted diphenylcyclopropene system was also studied in order to determine the preferred transition-state geometry for the rearrangement. The data obtained indicates that these systems proceed through a four-center, chair-like conformation. The thermal [2 + 2]-cycloaddition reactions to produce the tricyclohexane skeleton proceed with total inversion of stereochemistry about the olefinic π system. The reaction was shown to proceed via initial formation of a biradical intermediate in a conformation which is analogous to the conformation of cyclohexane. Ring inversion of the initially formed chair intermediate generates a boat diradical which undergoes subsequent coupling. The ring flip of the initially formed chair intermediate to the boat diradical is the major factor responsible for the overall inversion of stereochemistry. The results obtained indicate that the Cope rearrangement of the allyl-substituted cyclopropene system is not a true pericyclic process but rather involves the formation of an intermediate analogous to the 1,4-cyclohexylene biradical.

The Cope rearrangement of hexa-1,5-dienes[1] has been commonly regarded as a typical example of an orbital symmetry controlled sigmatropic reaction.[2,3] As a result of the elegant stereochemical labeling studies of Doering and Roth[4] and Hill,[5] the lowest energy Cope process has been accepted as that involving a chair transition state. It is, however, possible for the reaction to take place via the alternative boat conformation,[4,6] especially if the rearrangement is facilitated by relief of ring strain.[7-10] Despite intensive work,[11] the mechanism of the [3,3]-sigmatropic shift of 1,5-hexadienes remains unclear. Mechanistic considerations of the Cope rearrangement include (1) cleavage of the diene into two allyl radicals followed by

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