Photochemistry of Anthracene-9,10-endoperoxide

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The wavelength dependence of the photochemistry of anthracene-9,10-endoperoxide (APO) in acetonitrile was quantitatively investigated at 5 °C, with excitation varied from 240 to 450 nm. Anthracene (AC) and a diepoxide (DE) were identified as the main primary photoproducts. After short exposure times DE was at all wavelengths the dominating photoproduct, while AC was only formed for $\lambda \leq 320$ nm. The maximum AC quantum yield of 29% was reached at 270 nm. Anthraquinone (AQ) and a bicyclic acetal (BA) were identified as the main secondary products. Formation of AQ and BA occurred both from DE and from ground-state APO. Formation of BA from ground-state APO involved excited DE or BA itself, while formation of BA from DE required UV excitation of DE. Room-temperature thermolysis of APO only produced AQ. For $\lambda \leq 310$ nm the total photochemistry quantum yield was, within error margins, constant and close to unity. Between 300 and 450 nm, the tail of the APO absorption spectrum, a more or less monotonic decrease of the total photochemistry quantum yield was observed.

Introduction

Aromatic endoperoxides possess the capability to generate singlet oxygen ($^1O_2$) upon warming[1−4] or photoexcitation.[5−7] The highly reactive $^1O_2$ is utilized in the purification of wastewater,[8] photodynamic therapy,[9] and deactivation of viruses and bacteriae.[10] The possibility of endoperoxides to release this reactive species by unimolecular decomposition makes them interesting candidates for in vivo site-specific oxidative targeting[11] with $^1O_2$. Another interesting aspect is that many aromatic endoperoxides exhibit a dual mode of photochemistry.[7] For instance, for anthracene-9,10-endoperoxide (APO) it has been concluded that excitation to S_n, with $n \geq 2$, leads to cycloreversion, producing anthracene and $^1O_2$, whereas excitation to the S_1 state would initially cause homolytic O−O cleavage, eventually resulting in a diepoxide rearrangement product.[12]

Klein, Kalb, and Gudipati[13] were the first to present an assignment of the APO absorption spectrum based on semiempirical INDO/S and CNDO/S calculations. Recently, a revised assignment of the low-lying electronic states of APO in chloroform was presented by us,[14] based on a combination of MS-CASPT2/CASSCF calculations, absorption and emission spectroscopy, and femtosecond polarization-resolved spectroscopy. In this revised assignment the $S_0 \rightarrow S_1$ transition was found to be of $\pi^*_{OO} \rightarrow \sigma^*_{OO}$ character, similar to predictions by Kearns[15] for cyclopentadiene-1,4-endoperoxide but contrasting with Klein et al.[13,16] Moreover, emission was observed near 340 nm after excitation of APO in the UV, in contrast with a previous conclusion.[17] A peak at 291 nm in the emission excitation spectra was assigned to the $S_0 \rightarrow S_1$ transition,[14] associated with the O−O homolytic cleavage reaction pathway. This assignment was in agreement with new theoretical calculations[14] and can be compared to a weak first absorption maximum at 280 nm in the endoperoxide tetramethyldioxetane.[18] The location of the $S_0 \rightarrow S_1$ transition was before said to be below 23 000 cm^{-1} (equivalent to $\lambda \geq 435$ nm).[12,19] However, spectroscopic evidence supporting this was never presented. For instance, the shape of the absorption spectrum was never investigated for longer wavelengths than 400 nm.[12,19] The origin of the claim that the $S_0 \rightarrow S_1$ transition occurs below 23 000 cm^{-1} seems to be related to the photosynthesis of the diepoxide compound from APO by Rigaudy et al.[20] This photosynthesis was performed at 5−6 °C, by exposing a 20 mM solution of APO in dry benzene for 40 h to all light from a 1600 W xenon lamp, passed through a GG 455 cutoff filter, resulting in the diepoxide product with a 78% conversion yield. Rigaudy et al.[20] further remarked that at wavelengths shorter than 435 nm mainly anthraquinone and its derivatives were generated.

Since the inability to photochemically synthesize the diepoxide compound with $\lambda \leq 435$ nm appears to be the main existing support for putting the location of the $S_0 \rightarrow S_1$ transition at $\lambda \geq 435$ nm, we decided to perform a wavelength-dependent investigation of the photochemistry of APO in acetonitrile, with excitation varied from 240 to 450 nm, using absorption and ^1H NMR spectroscopy to identify and quantify the main reaction products. In particular, we determined the wavelength dependence of absolute photochemistry quantum yields of the various reaction products over the excitation region of 240−450 nm. Kinetics of the photoproduct build up was also monitored at selected wavelengths and reveals additional information on pathways in APO photochemistry.

Experimental Section

Anthracene-9,10-endoperoxide (APO) was synthesized as described elsewhere.[14] Antraquinone, anthracene, spectrophotometric- and HPLC-grade acetonitrile, and perdeuterated acetonitrile were all purchased from Sigma-Aldrich and used as received.

Absorption experiments were performed on a Shimadzu UV-1601PC and a Cary 100 UV−visible absorption spectrometer.

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Wavelength-dependent photochemical conversion of APO in acetonitrile at 5 °C was accomplished using a Spex Fluoromax-3 system, equipped with a 150 W xenon lamp, as a tunable and stable excitation source. The samples were continuously stirred during the irradiation process. The sample volumes were typically 3.0 mL and contained APO in a concentration of 0.2 or 0.5 mM. Exposure periods were typically 5−20 min, guaranteeing a negligible contribution to the reaction products from thermolysis. In addition, we took 15 consecutive absorption scans on a single sample to verify that photoproduct generation due to the recording of absorption spectra could be neglected. To compensate for the low photon absorption at wavelengths longer than 290 nm the photon flux in the Fluoromax-3 system was gradually increased by changing the excitation bandwidth from 4 nm for $\lambda \leq 290$ nm to 10 nm at 370−400 nm. The measurement at 450 nm was done with 20 nm excitation bandwidth and a single-exposure period of 30 min. Appropriate cutoff filters were used at the exit of the excitation monochromator for excitation with $\lambda \geq 300$ nm to make certain that no light of shorter wavelengths comes through from higher orders of the monochromator. At each excitation wavelength Rayleigh spectra of a cuvette filled with water were recorded for 4 nm excitation bandwidth and for the bandwidth/cutoff filter combination used in the actual excitation process. This way the increase in photon flux due to a changed excitation bandwidth/cutoff filter combination was determined.

Identification of reaction products was accomplished by decomposition of the absorption spectra using spectra of the available pure compounds in acetonitrile and further verified by analysis of ^{1}H NMR spectra of partially photochemically converted samples of APO in acetonitrile with starting concentrations of 0.6−5.7 mM APO. The ^{1}H NMR spectra were measured using a Bruker AMX 500 spectrometer.

Absolute quantum yield measurements were performed with excitation around 290 nm on samples with concentrations of 0.2 or 0.5 mM. Laser pulses centered near 290 nm, with a 1 kHz repetition rate, were created by sum and difference frequency generation from the output of an amplified Ti:Sa laser system (Coherent USP-1), resulting in 0.6−1.4 mW output at 290 nm.

Kinetic studies of the photoproduct build up were carried out either with laser excitation at 23 °C or in the Fluoromax-3 system at 5 °C.

Results and Discussion

a. Accurate Determination of the APO Absorption Spectrum. Figure 1 demonstrates the wavelength dependence of the extinction coefficient of our APO in acetonitrile samples over the region of 200−600 nm, after correcting for the acetonitrile absorption. Absorption spectra from samples with APO concentrations ranging from 45.4 μM to 24.0 mM were combined to generate this spectrum. The APO concentration differed by a factor 2−3 for consecutive samples in this series. In contrast to our previous investigation,[14] instead of chloroform, acetonitrile was chosen as solvent, because of its low absorption over this entire wavelength range. Chloroform absorbs strongly below 250 nm, and in addition, we observed that excitation near 250 nm leads to a chemical reaction between chloroform and anthracene, in line with ref 21. Furthermore, chloroform is known as an unstable solvent that generates free radical degradation products and therefore typically contains stabilizers such as the free radical scavenger amylene. Acetonitrile, on the other hand, is a stable solvent under ordinary conditions of use. The absorption peaks seen between 500 and 600 nm in Figure 1 are not related to APO but represent absorption of the residual presence of ∼1.2 ppm palladium tetra(*tert*-butyl)porphyrazine, the photosensitizer used in the photochemical synthesis of APO from anthracene and oxygen,[14] as can be verified by comparison to the absorption spectrum of this photosensitizer in acetonitrile. Below 500 nm the contribution of this compound to the absorption spectrum is negligible. The absorption spectrum in Figure 1 shows APO absorption maxima (final state; extinction coefficient) at 277.5 (S_2; $\epsilon = 500 \pm 30$), 269.5 (S_4; $\epsilon = 625 \pm 40$), and 216.5 nm ($\epsilon = 44\,000 \pm 3000$). Detailed knowledge about the APO absorption spectrum is essential in extracting the absolute photochemistry quantum yields and relative emission quantum yields.

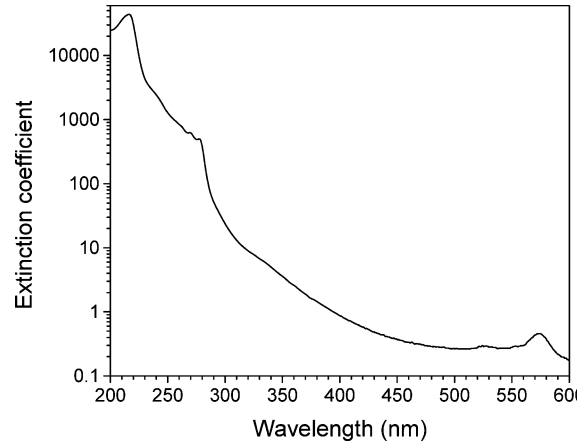


Figure 1. Spectral dependence of the extinction coefficient of our anthracene-9,10-endoperoxide (APO) in acetonitrile samples at room temperature, created from a dilution series with APO concentrations ranging from 24.0 mM to 45.4 μM. In each dilution step the concentration was reduced 2−3 times. Absorption peaks in the region 500−600 nm are from a residual ∼1.2 ppm of the photosensitizer palladium tetra(*tert*-butyl)porphyrazine, used in the synthesis of APO from anthracene and oxygen.

b. Identification of the Main Photoproducts. In Figure 2a difference spectra (after exposure − before exposure) are shown for photochemical conversion at 5 °C for four different excitation wavelengths. Four main products can be identified: anthracene, anthraquinone, a diepoxide (*syn*-anthracene 4a,10:9,9a-dioxide[20]), and a bicyclic acetal. Absorption spectra for these compounds are shown in Figure 2b, and their chemical structure is shown in Scheme 1, which summarizes most of our findings. For the spectral decomposition, accurate absorption spectra were recorded for pure solutions in acetonitrile of anthracene (first absorption peak at 375.5 nm, $\epsilon = 6300 \pm 300$) and anthraquinone (first absorption peak at 323 nm, $\epsilon = 4600 \pm 200$).

The spectrum of the diepoxide (DE) and its extinction coefficient were determined by combining absorption spectra and ^{1}H NMR spectra of partially photochemically converted samples of APO (initial APO concentrations of 0.6 and 5.2 mM; see Table 1) in perdeuterated acetonitrile. These ^{1}H NMR spectra are shown in Figure 3, and details of the various identified chemical compounds in these samples are listed in Table 1. The DE spectrum shown in Figure 2b is very reliable down to 290 nm, due to little absorption by APO and the other photoproducts. Below 290 nm the general shape is still reliable, but the error margins gradually increase due to increased absorption by APO and anthraquinone. Rigaudy et al.[20] reported the following absorption maxima with log(ϵ) values for DE in diethyl ether: 284.5 (3.49), 278.5 (3.51), and 273 nm (3.48), unfortunately without showing the actual absorption spectrum. Our DE absorption spectrum (see Figure 2b) has a maximum at 283 nm

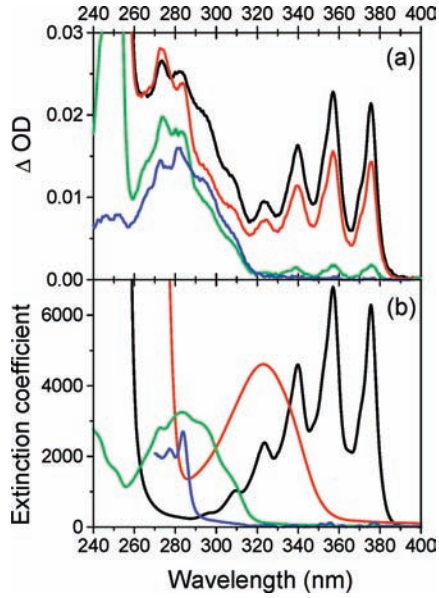


Figure 2. (a) Difference spectra for samples of 0.2 mM anthracene-9,10-endoperoxide in acetonitrile for photoexcitation at 270 (black), 290 (red), 310 (green), and 330 nm (blue). (b) Spectral dependence of the extinction coefficient of the four main identified reaction products: anthracene (black), anthraquinone (red), diepoxide (green), bicyclic acetal (blue).

($\log(\epsilon) = 3.51$), with a second peak at 273 nm (3.45), and shoulders are seen around 292 and 308 nm. Overall the agreement with the absorption data listed by Rigaudy et al.[20] is reasonable. Comparison of our ^{1}H NMR spectra of partially photochemically converted samples of APO in perdeuterated acetonitrile (see Figure 3) to the NMR data of Rigaudy et al.[20] provides indisputable confirmation that indeed the diepoxide was formed. The largest deviation from Rigaudy et al.'s[20] chemical shift values for DE in $CDCl_3$ is for the H-9,10 signal, which we found at $\delta = 4.15$ instead of $\delta = 4.07$. Note that use of a different solvent and temperature can lead to some deviations in δ values. Furthermore, the integral of the $\delta = 7.46$ (H-6,7) peak cannot be determined here because of overlap with a strong APO peak at $\delta = 7.49$.

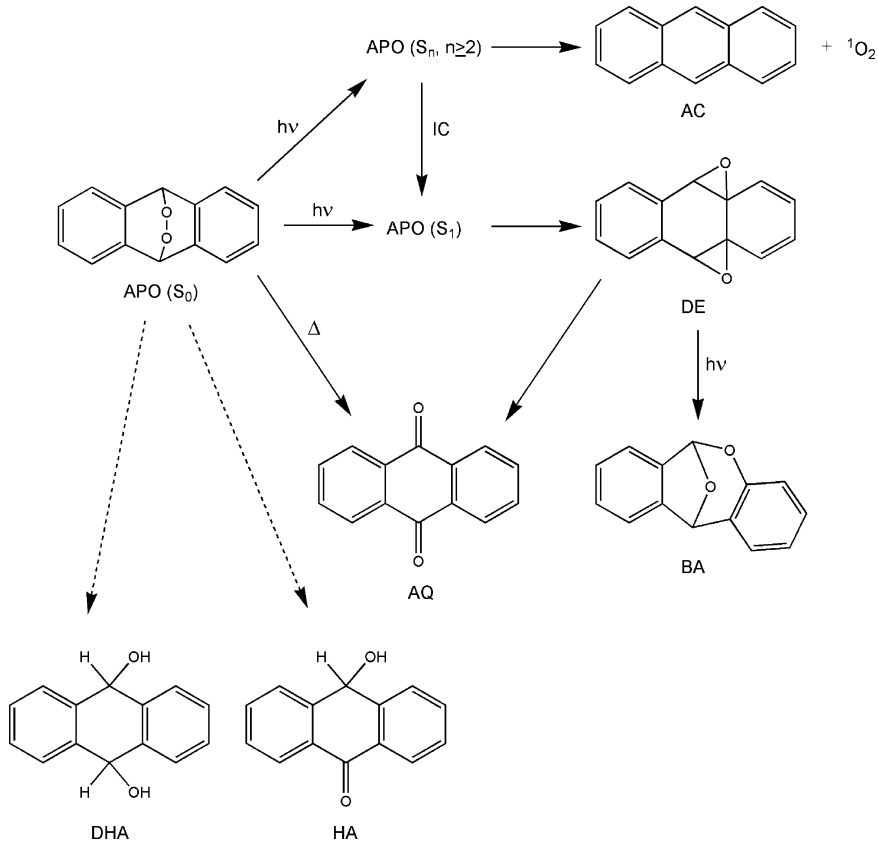
The presence of a bicyclic acetal as photochemical product is most prominent in difference spectra obtained with photoexcitation in the region 280−310 nm and is characterized by the appearance of a peak at 283.5 nm (e.g., see the red spectrum in Figure 2a). ^{1}H NMR was used also in the identification of this compound, for which a 1.0 mM APO sample was partially photochemically converted by 110 min irradiation with 290 nm laser pulses (0.9 mW). Again, ^{1}H NMR peak positions (see Figure 3) were in agreement with those found by Rigaudy et al.,[20] and peak integrals were in accordance with the number of protons associated with the peaks. The composition of this sample is also listed in Table 1. The bicyclic acetal absorption spectrum shown in Figure 2b is not very reliable below 280 nm. According to Rigaudy et al.,[20] in diethyl ether this compound has absorption maxima ($\log(\epsilon)$) at 285.5 (3.52) and 278 nm (3.48), the first peak about 2 nm red shifted from our 283.5 nm (3.43 ± 0.05) peak, which is the only one considered reliable here.

c. Wavelength Dependence of the Photochemistry Quantum Yields. A series of photochemical conversion experiments was performed at 10 nm intervals between 240 and 400 nm and at 450 nm to determine the wavelength dependence of the various photochemistry quantum yields (QY's). The photochemistry quantum yield of reaction product X is defined as the number of molecules X generated, divided by the number of photons absorbed by APO molecules. A total photochemistry QY of 100% implies that every excitation leads to a photoproduct molecule. Furthermore, excited-state absorption or 2-photon absorption would reduce the observed maximum total photochemistry QY to less than 100%, since in these situations at least two photons were absorbed to produce a single photoproduct molecule. The excitation was performed with a Fluoromax-3 system, which provided us with a reliable low-intensity tunable and stable excitation source, and consequently, multiphoton effects can be excluded. In combination with accurate knowledge of the APO absorption spectrum this allows for the extraction of relative QY's for the various photoproducts from spectra like those shown in Figure 2a. Conversion of these results to absolute QY's was accomplished by determining the absolute QY of anthracene (AC) formation at 290 nm and scaling all relative QY's to this value. The results from five such absolute QY determinations, using 0.6−1.4 mW pulsed excitation on 0.2 and 0.5 mM samples, were found to vary between 18.7% and 21.6%, from which we conclude a QY of $20 \pm 2\%$ for AC formation with excitation at 290 nm. Main sources for errors in this QY determination are the AC extinction coefficient (accuracy $\pm$ 5%), fluctuations in the laser power during the 10−20 min exposure (~5−10%), and reliability of the calibration of the laser power meter. In our opinion, these error sources warrant a larger error margin than expressed in the variation of our results.

The most significant results are presented in Figure 4, which shows the wavelength dependence of the absolute quantum yields of the different photochemical products, determined after a single (solid symbols) and double (open symbols) exposure period. In these experiments 1.7−15% of the starting amount of APO was photochemically converted after the second exposure period. Absolute quantum yield measurements for the AC formation were previously performed by Schmidt et al.[12] for APO in CH_2Cl_2. They concluded that the quantum yield for AC formation, associated with the cycloreversion reaction, reaches a maximum of 22% at 270 nm and drops to 1.5% at 313 nm.[12] In general, our AC formation QY's in acetonitrile, depicted in the top panel of Figure 4, show the same trend as observed by Schmidt et al.[12] in CH_2Cl_2 but are somewhat higher, with a maximum of 29% at 270 nm, which corresponds to the absorption maximum of the $S_0 \rightarrow S_4$ transition.[14] At 320 nm the antracene QY has dropped to 0.35%, and at longer wavelengths no detectable amount of AC is generated. The fact that the anthracene QY clearly drops at both shorter and longer wavelengths than 270 nm indicates that the cycloreversion reaction is significantly more efficient from the S_4 state than from other nearby electronic states. In addition, it makes it unlikely that the 270 nm peak is a vibronic transition related to the 277.5 nm electronic transition, in agreement with theoretical results published by us.[14] Given the conclusion by Klein et al.[13,16] that with 275 nm excitation the only photolysis product for APO in argon matrices at 22 K is anthracene, the photochemistry of APO may well be temperature and environment dependent.[16]

The second panel of Figure 4 shows the wavelength dependence of the diepoxide (DE) quantum yield. The most important result shown in this panel is that at all wavelengths between 240 and 400 nm there is a significant QY for DE, varying from 30% to almost 80%. This result is in sharp contrast with the result of Rigaudy et al.[20] that DE cannot be synthesized at wavelengths shorter than 435 nm. As mentioned, this seems to be the only experimental basis for the claim[12,19] that the $S_0 \rightarrow S_1$ transition is situated above 435 nm. The diepoxide QY data

SCHEME 1: Overview of Photochemical Reaction Pathways Identified and Discussed in the Present Work[a]



[a] IC stands for internal conversion, and the other abbreviations stand for anthracene-9,10-endoperoxide (APO), bicyclic acetal (BA), antraquinone (AQ), diepoxide (DE), anthracene (AC), 9,10-dihydroxy-9,10-dihydroanthracene (DHA), and 9-hydroxy-10-anthrone (HA). Dotted lines indicate insufficient knowledge about the exact reaction pathways leading to these products.

TABLE 1: Composition of Partially Photochemically Converted Anthracene-9,10-endoperoxide (APO) Samples, Investigated with ^{1}H NMR, Corresponding to the Spectra in Figure 3[a]

excitation, λ (nm)	T (°C)	$[APO]_{t=0}$ (mM)	APO (%)	BA (%)	AQ (%)	DE (%)	AC (%)	DHA (%)	HA (%)
289	23	1.0	58.4	22.8	10.7	2.2	4.7		
360	5	0.6	77.0		2.7	20.3			
360	5	5.2	85.1		3.4	10.4		0.9	
350	5	5.7	81.0		4.0	8.8		2.5	2.7

[a] The first three columns list the excitation wavelengths, temperature, and initial APO concentrations of the samples. The other columns list the molar percentages of APO and the identified products after photoconversion. The identified products are a bicyclic acetal (BA), antraquinone (AQ), a diepoxide (DE), anthracene (AC), 9,10-dihydroxy-9,10-dihydroanthracene (DHA), and 9-hydroxy-10-anthrone (HA). At most 1.2% of the ^{1}H NMR signal integrals belongs to unidentified compounds.

in Figure 4 clearly demonstrate that this claim has now become untenable. Our results also agree with conventional wisdom:[22] Typically, for states S_n with $n \geq 2$ photochemistry is expected to compete with rapid internal conversion to S_1. Since it has generally been accepted that excitation to the APO S_1 state leads to homolytic cleavage of the peroxide bridge and both we and Schmidt et al.[12] conclude that the other photochemical reaction channel (cycloreversion to anthracene and singlet oxygen) always has a QY below 30%, it follows that at least 70% of the excited-state population will probably end up in the S_1 state, prior to consecutive further decay and photochemical conversion. At 450 nm, with 20 nm excitation bandwidth, we still obtained a diepoxide QY of ~16%, confirming Rigaudy et al.'s[20] result that the DE can be synthesized at these wavelengths, albeit with an efficiency more than three times lower than at 360 nm. Although one cannot conclude the position of the $S_0 \rightarrow S_1$ transition from the data in the second panel, the argument can be made that the clear drop in the DE quantum yield with excitation above 380 nm indicates that this absorption should occur at $\lambda \leq 380$ nm. As mentioned above, in our previous work[14] we concluded that the $S_0 \rightarrow S_1$ transition is at 291 nm for APO in chloroform.

In the region 270−310 nm, the diepoxide QY shows a clear dip, compared to both shorter and longer wavelengths. Moreover, particularly the data at 280−300 nm gave a significantly higher diepoxide QY after a single irradiation period than after the double exposure time. As the DE absorption spectrum in Figure 2b shows, the DE has significant absorption in this wavelength region, with initially little competition of the other compounds, whereas below 280 nm initially DE absorption has to compete with APO and at later stages with the other photoproducts. These data therefore clearly suggest that absorption of light by DE reduces the diepoxide QY. The diepoxide QY also shows a decreasing trend at wavelengths longer than 310 nm. However, in this wavelength region no significant

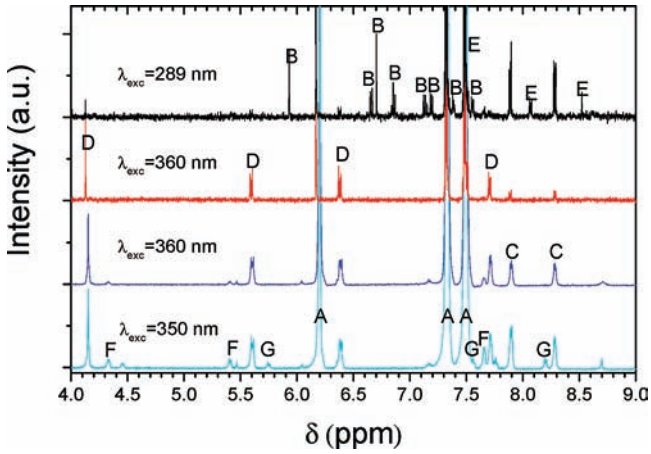


Figure 3. ^{1}H NMR spectra of partially photochemically converted samples of anthracene-9,10-endoperoxide (APO) in perdeuterated acetonitrile. From top to bottom, the sample's initial APO concentration, excitation wavelength, and sample temperature were as follows: 1.0 mM, 289 nm, 23 °C; 0.6 mM, 360 nm, 5 °C; 5.2 mM, 360 nm, 5 °C; and 5.7 mM, 350 nm, 5 °C. The peak positions of identified compounds are labeled (A) APO, (B) bicyclic acetal, (C) antraquinone, (D) diepoxide, (E) anthracene, (F) 9,10-dihydroxy-9,10-dihydroanthracene, and (G) 9-hydroxy-10-anthrone. The quantitative composition of identified compounds in the samples can be found in Table 1.

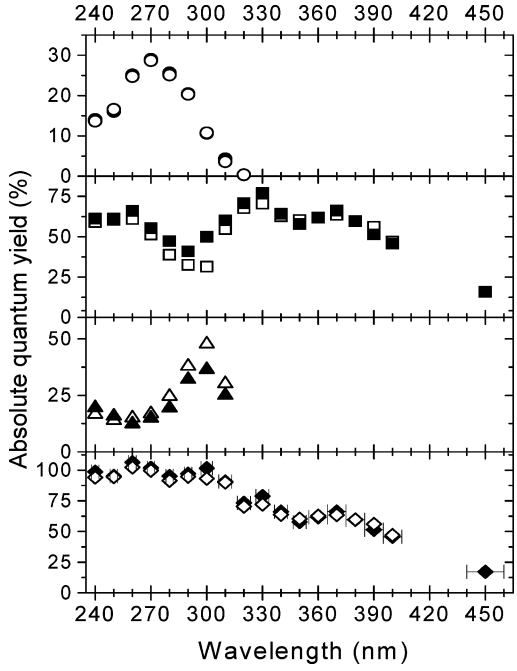


Figure 4. Absolute photochemistry quantum yields as a function of excitation wavelength for, from top to bottom, anthracene, diepoxide, bicyclic acetal, and all photoproducts combined (including anthraquinone). The solid symbols correspond to the yields after a single exposure period, whereas the open symbols are the yields determined after the double exposure period. The horizontal bars to the data points in the lowest panel indicate the excitation bandwidth used at the various excitation wavelengths.

difference is seen between the diepoxide QY after the first and second exposure periods.

The third panel of Figure 4 shows the wavelength dependence of the bicyclic acetal QY. The QY for this compound is much higher in the region 280−310 nm than in the region 240−270 nm, and between 280 and 310 nm these QY's also become significantly higher after the second irradiation period. Consequently, these data demonstrate that optical excitation of the DE leads to formation of the bicyclic acetal. Rigaudy et al.[20] previously reported that addition of protic or Lewis acids (e.g., $ZnCl_2$) to solutions of the DE transforms DE to the bicyclic acetal. On the other hand, for 9,10-diphenylanthracene-9,10-endoperoxide Rigaudy et al.[5] concluded that optical excitation of the corresponding diepoxide led to formation of a bicyclic acetal. Our results clearly demonstrate that the latter process also occurs for the diepoxide created from APO.

The wavelength dependence of the anthraquinone QY is not shown. At all wavelengths the anthraquinone QY was very low in this particular series of experiments, varying from 0% to 6% without a clear trend. On the basis of our data at room temperature, thermolysis of APO (vide infra) could have contributed less than 1% to the anthraquinone QY during the time it took to perform these experiments. Because for $\lambda > 320$ nm DE is the only other product, we conjecture that the observed anthraquinone (AQ) mostly has DE as precursor. AQ was also a minor byproduct (2−6%) in Rigaudy et al.'s[20] original synthesis of the diepoxide. On the other hand, we found that in the thermolysis of APO at room temperature AQ is virtually the only product. This again is very different from the reported thermolysis of APO in boiling benzene, toluene, or *o*-dichlorobenzene (temperatures 80−110 °C), where the AQ yield was 10% at most and the bulk of the APO had been converted to dimers.[23] Schmidt and Brauer[17] also reported thermolysis experiments on endoperoxides of aromatic hydrocarbons at 139 °C. They determined only the formation QY A_c of the parent hydrocarbons and inferred that the quantum yield of all other rearrangement products together is $1 - A_c$, without analyzing what these products are. In the case of APO they deduced a 99% QY for rearrangement products,[17] in line with our results on APO thermolysis at room temperature.

The thermal decomposition of APO at 23 °C was followed by us for 1−2 weeks for APO samples in three different types of acetonitrile. For APO in perdeuterated acetonitrile and spectrophotometric-grade acetonitrile, AQ was found to be the only thermal end product, but it was formed about 8 times faster in the perdeuterated acetonitrile. In perdeuterated acetonitrile about 70% of the APO was converted to AQ after 6 days, and extrapolation of the single-exponential fit predicts 100% final conversion, indicating that this conversion process is unimolecular. In HPLC-grade acetonitrile, on the other hand, no noticeable thermal conversion was detected even after 2 weeks, and therefore, the differences in thermal conversion rates most likely are determined by various residue compounds present in commercial-grade solvents rather than by an isotope effect. An extensive investigation of thermolysis of endoperoxides of aromatic compounds has been performed by Turro et al.[3,4] They investigated, among others, thermolysis of 9,10-diphenylanthracene-9,10-endoperoxide and the 1,4-dimethyl derivative.[3,4] Interestingly, thermolysis of these compounds proceeds substantially via the cycloreversion pathway,[3,4] producing $^1O_2$ in an endothermic reaction, in some cases with yields as high as 95%.

The thermal evolution of the 5.7 mM APO sample, partially converted with 350 nm light (see Table 1), was also followed for 2 h with ^{1}H NMR at 55 °C. In these spectra the DE concentration dropped more than 70% during this time, and a best single-exponential fit indicates a decay time of 0.67 h, which can be compared to a half-lifetime of 6.5 h (= decay time of 9.4 h) at 28 °C, reported by Rigaudy et al.[20] At higher temperatures several new thermal products were formed,

increasing the complexity of the kinetics even further, and therefore, we cannot conclude which products DE evolves into in this case.

The last panel in Figure 4 shows the total photochemistry QY (i.e., including AQ) as a function of excitation wavelength. At wavelengths $\lambda \leq 310$ nm the total photochemistry QY is roughly constant and close to unity, given a realistic error margin of ±15%. Between 300 and 450 nm, on the other hand, a fairly linear decline of the total photochemistry QY is observed from ~100% at 300 nm to ~17% at 450 nm. The drop in photochemistry QY cannot be explained by the emission we observed[14] from APO, with a first maximum at 340 nm. By comparison to the emission yield for anthracene (reported QY ≈ 30%; see refs 24 and 25), we estimate that the QY of this emission is less than 1%, and therefore, it represents a negligible excited-state decay channel.

In standard line broadening models, applicable for low-temperature solid samples, the absorption line shape is a convolution of a dynamic Lorentzian homogeneous line shape component (optical dephasing in Markovian limit), with a static inhomogeneous Gaussian broadening profile.[26] In such models, Lorentzian profiles should dominate the line shape far out in the spectral wings, and therefore, emission and photochemistry QY's are expected to reach constant values, conflicting with the steady decline observed here. The presence of other weak absorption bands, for instance, related to singlet−triplet transitions, may change this picture. If direct singlet−triplet absorption would increasingly contribute to the long wavelength tail of the APO absorption spectrum, the smooth decline in total photochemistry QY shown in Figure 4 would indicate a lower APO photochemistry quantum yield from triplet states than from singlet states. Alternatively, it seems relevant to consider that the standard separation of static Gaussian and dynamic Lorentzian contributions to the absorption profile does not generally hold in liquid solutions.[26,27] Therefore, the observed steady decline with lower excitation energy could indicate that the molecules associated with absorption further out in the wings gradually are more likely to obtain insufficient energy for overcoming energy barriers that would result in photochemistry. The most probable competing decay channel, responsible for the drop in photochemistry QY, is internal conversion to the APO electronic ground state. Note that the excitation energy at 450 nm is ~13 800 cm^{-1} below the lowest optically discernible absorption maximum in APO at 277.5 nm (~36 000 cm^{-1}), and the extinction coefficient at this wavelength is about 3 orders of magnitude lower than at 277.5 nm (cf. Figure 1). We are unaware of any other investigations of photochemistry QY's extending this far into the wings of a molecular absorption spectrum and as such cannot state whether the observed behavior represents an anomaly or a general feature of photochemistry in solvents.

d. Kinetics of Photoproduct Formation during Irradiation at Selected Wavelengths. The kinetics of photoproduct build up during prolonged excitation was also followed over about 100−140 min for three different excitation wavelengths, i.e., 289, 327, and 360 nm. This kinetics is shown in Figure 5. With excitation at 360 nm, predominantly DE was created, with AQ as a minor byproduct. For presentation purposes in Figure 5c the AQ yield has been multiplied by 10. The composition, as determined by ^{1}H NMR, of this initially 0.6 mM APO sample after 140 min exposure is listed in Table 1. With 23% of the APO converted, the DE yield is 88%, implying that higher chemical reaction yields than the 78% achieved by Rigaudy et al.[20] are in principle possible. Also, with excitation at 327 nm

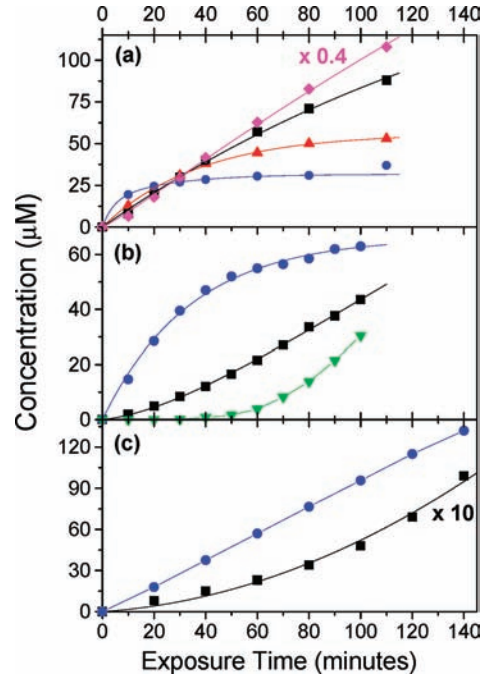


Figure 5. Photochemistry kinetics of various reaction products. Excitation was performed with laser light at (a) 289 (fwhm 4.3 nm; initially 1.0 mM APO; 23 °C) and (b) 327 nm (fwhm 2.5 nm; initially 0.22 mM APO; 23 °C) and (c) with the Fluoromax-3 system at 360 nm (fwhm 15 nm; initially 0.6 mM APO; 5 °C). The final composition of the 289 and 360 nm samples, as determined by ^{1}H NMR, are the first two listed in Table 1. The identified photoproducts are anthracene (▲), diepoxide (●), anthraquinone (■), and the bicyclic acetal (♦). The rise of the absorption of an unidentified product (▼), created with 327 nm exitation, is also plotted. The OD of this component at 269 nm was 0.15 after 100 min irradiation.

the photoproducts were predominantly DE and AQ. However, after 40 min, when about one-quarter of the APO had been converted, a third component started to make its appearance in the absorption spectra, with a broad absorption band starting below 290 nm and a maximum at 269 nm (spectrum not shown). The late appearance and exponential rise of the absorption of this unidentified component point to a product from a bimolecular reaction, and AQ must be one of the starting compounds, because the exponential rise requires a compound whose concentration still increases significantly after 40 min exposure. Fitting the kinetics with various reaction schemes is unfortunately inconclusive in determining whether the second reaction component is APO or DE.

Excitation at 289 nm results in even more complex photochemistry. The dominating product is now the bicyclic acetal (BA). For presentation purposes in Figure 5a its yield is scaled down by a factor 0.4. Initially the increase of the AQ yield is proportional to the BA yield but clearly starts to deviate after 40 min. The DE concentration is already after 20 min close to its plateau value of ~30 μM, which is about one-half the plateau concentration reached with 327 nm excitation and more than four times less than the DE concentration after 100 min conversion with 360 nm light. In the discussion of the absolute QY data of Figure 4 we already established that excitation of DE leads to formation of BA. Obviously this process is very efficient and therefore severely reduces the maximum concentration of DE that can be attained, despite the fact that the sample exposed to 289 nm initially had the highest APO concentration. The trend seems clearly that higher DE concentrations can be obtained with longer excitation wavelengths.

TABLE 2: Time Constants (in hours) for Antraquinone (AQ) and Bicyclic Acetal (BA) Formation from Diepoxide (DE) and Ground State APO, Obtained through Kinetic Analysis of the Data in Figure 5, and from Thermolysis

λ (nm)	T (°C)	$\tau_{APO\rightarrow AQ}$ (h)	$\tau_{DE\rightarrow AQ}$ (h)	$\tau_{APO\rightarrow BA}$(h)	$\tau_{DE\rightarrow BA}$ (h)
289	23	15		9.1	0.41
327	23	35	2.0		
360	5	830	20		
thermal	23	120[a]/>930[b]/c			

[a] In perdeuterated acetonitrile. [b] In spectrophotometric grade acetonitrile. [c] No AQ yet after 2 weeks in HPLC grade acetonitrile.

Another interesting issue to notice is that the QY of AC after the total 110 min of 289 nm exposure is only 11.3% (cf. Table 1), approximately one-half the value determined in our five absolute QY determinations for AC at 290 nm. As the data in Figure 4 clearly demonstrated that at all wavelengths the AC formation QY does not change with prolonged exposure, the build up of AC in time in Figure 5a can be regarded as a measure for the photochemical consumption of APO by optical excitation of APO. The overall reduction of the AC QY therefore indicates that the APO concentration now has also been reduced by reactions that do not involve optical excitation of APO. Since unimolecular thermal decomposition can also be ruled out (vide supra), the conclusion must be that formation of BA, and perhaps also AQ, potentially also proceeds via a bimolecular mechanism with ground-state APO, thereby causing nearly a doubling of the APO consumption rate. Considering only the final BA and AC concentrations (so ignoring AQ and DE) gives a final AC QY of 17%, already less than the 20% determined by us, and therefore, some of the BA formation is for certain accompanied by additional consumption of ground-state APO. Note further that the total photochemistry QY is close to unity (see Figure 4), and therefore, any reaction between a photoproduct and excited-state APO would not lead to extra APO consumption.

The AQ and BA formation kinetics in Figure 5 was further analyzed by assuming two first-order kinetics feeding channels: one proportional to the APO concentration and not involving DE as an intermediate, and one proportional to the DE concentration. The extracted time constants are gathered in Table 2. At 327 and 360 nm the time constants indicate that AQ formation from DE is more than an order of magnitude faster than from APO; the same is observed at 289 nm for BA. Moreover, both AQ formation rates seem to become faster at shorter wavelengths, suggesting UV absorption may accelerate the AQ formation. Note, however, that the rates for 360 nm excitation are also expected to be slower because this conversion was performed at a lower temperature (5 versus 23 °C). Nevertheless, this observation does provide an explanation for Rigaudy et al.'s[20] inability to synthesize DE with excitation at $\lambda \leq 435$ nm. Their result that mainly AQ and its derivatives are obtained at shorter wavelengths[20] corroborates our suggestion that excitation of DE promotes the conversion to AQ. Furthermore, we noticed that the AQ yield increased dramatically at the expense of the DE yield if the sample was not stirred during the irradiation process.

With 289 nm excitation we found a time constant for formation of BA from DE but could not determine one for AQ formation from DE, which implies that at this wavelength DE is converted to BA only. On the basis of the fits of the 289 nm kinetics, after 110 min ~53% of the converted APO has generated, without involvement of DE as an intermediate, all AQ, and ~55% of the BA. If we would assume that these amounts of AQ and BA are completely generated without optical excitation of APO, then only ~47% of the APO would have been photochemically converted. In this case, the above-mentioned 11.3% AC yield after 110 min 289 nm excitation would actually imply a 25% AC QY created through UV excitation of APO, a value somewhat higher than the 20 ± 2% we determined. To arrive at an AC QY of 20%, one-quarter of the ~53% APO converted without the diepoxide intermediate still needs to be generated through UV excitation of APO. Given our kinetics results with 327 and 360 nm excitation, it is unlikely that none of the AQ is formed from DE, even though the fitting procedure did not reveal this. Moreover, because at 327 and 360 nm BA was not observed, it can further be concluded that ground-state APO, ground-state DE, and ground-state AQ, neither by themselves nor combined, can result in BA formation. The (bimolecular) isomerization of ground-state APO to BA under 289 nm illumination must therefore be catalyzed by either excited-state DE or the BA itself.

The possibility of bimolecular reaction pathways affecting the (photo)chemistry outcome is also demonstrated by analysis with ^{1}H NMR of two more concentrated APO samples, partially converted at 5 °C with excitation at 350 and 360 nm, respectively. Their ^{1}H NMR spectra are also shown in Figure 3, and their composition is listed in Table 1. With excitation at 360 nm the DE yield dropped from 88% in the 0.6 mM sample to 70% in the 5.2 mM sample and decreased even further to 46% with excitation at 350 nm in a 5.7 mM sample. At the same time the AQ yield changed from 12% to 23% and 21%, respectively, for these three samples. In addition, several new peaks appeared in the ^{1}H NMR spectra (cf. Figure 3). Three of these, seen in both the 350 and 360 nm converted samples, are tentatively assigned by us to 9,10-dihydroxy-9,10-dihydroanthracene (DHA), a compound not mentioned in previous work on the photochemistry of APO.[7,12,20,23] Even though ^{1}H NMR data for this compound[28] in perdeuterated DMSO at 110 °C do not exactly match our δ values at 5 °C in perdeuterated acetonitrile, the intensity ratio of the three identified peaks in both samples matches the expected intensity ratio, verifying that these three peaks belong to the same compound. Moreover, in investigations of the photochemistry of anthracene on dry silica and fumed silica surfaces[29] with excitation at 350 nm, next to APO, AQ, and four different dimeric products, 15% of the photoproducts was found to be DHA, and 7−8% was identified as 9-hydroxy-10-anthrone (HA). The latter compound was also identified in our 5.7 mM APO sample, photoconverted with 350 nm excitation, and its ^{1}H NMR peaks matched δ values reported by Rigaudy and co-workers.[23] Because DHA contains two more hydrogen atoms than APO or AC, it is clear that formation of this compound is only viable through a bimolecular mechanism. In fact, it is interesting to note that in Dabestani et al.'s[29] experiments the yields of DHA and AQ, which has two hydrogen atoms less, are similar. Sigman et al.[30] noted for the 350 nm photochemical conversion of anthracene in water that with 10% of the anthracene converted only APO and AQ had been formed, whereas after 70% conversion also minor fractions of DHA and HA were found in equal amounts. It can therefore be concluded that DHA and HA are formed more with increasing APO concentrations. A summary of some of our findings on the photochemistry of APO is depicted in Scheme 1.

Conclusions

At all wavelengths over the investigated excitation range of 240−450 nm the diepoxide (DE) was found to be the dominant

primary photoproduct of optically excited anthracene-9,10-endoperoxide (APO) in acetonitrile. This product, associated with the homolytic O−O cleavage pathway, is according to the literature[12] reached through the lowest optically excited singlet state of APO, the S_1 state. Our results demonstrate that photosynthesis of the diepoxide[20] is not limited to excitation at $\lambda \geq 435$ nm, which therefore no longer provides support for the claim[12,19] that the APO $S_0 \rightarrow S_1$ absorption lies at $\leq 23\,000$ cm^{-1}. The quantum yield of anthracene (AC), the primary photoproduct of the cycloreversion reaction channel, associated with excitation of S_n with $n \geq 2$, is highest for 270 nm excitation (29%), coinciding with the location of the $S_0 \rightarrow S_4$ transition.[14] Qualitatively the wavelength dependence of the AC yield is in accordance with previous work on APO in CH_2Cl_2 by Schmidt et al.[12] No detectable AC was created at wavelengths longer than 320 nm. With excitation wavelengths $\lambda \leq 310$ nm, optical excitation of DE was concluded to result in efficient isomerization of DE into a bicyclic acetal (BA). Photoproduct kinetics with excitation at 289 nm further reveals BA is also directly created from ground-state APO, presumably through a bimolecular reaction involving optically excited DE or BA. Anthraquinone (AQ) was found to be a minor secondary product after short exposure times. Thermolysis of APO at room temperature, on the other hand, resulted in AQ as the only detected product. Analysis of photoproduct kinetics with 327 or 360 nm excitation shows that AQ is created both from DE and from ground-state APO, with creation from DE about an order of magnitude faster. Partial conversion with 350 or 360 nm excitation of more concentrated 5.2 and 5.7 mM APO samples led to additional products resulting from bimolecular reactions. One of these, 9,10-dihydroxy-9,10-dihydroanthracene, is most likely created together with AQ in a single bimolecular reaction. The overall QY of all photoproducts together is, within error margins, close to unity for excitation at $\lambda \leq 310$ nm. In the range of 300−450 nm, where the optical density drops about a factor 10^3 below the lowest discernible APO absorption maximum at 277.5 nm ($S_0 \rightarrow S_2$ transition), a roughly monotonous decrease of the total photoproduct QY was observed, indicating that internal conversion to the APO electronic ground state starts to compete more efficiently with photochemistry in the tail of the absorption spectrum.

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