

Wavelength Dependent and Adiabatic Photochemistry of Endoperoxides of Aromatic Hydrocarbons

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The photochemical cleavage of the endoperoxides of anthradichromene and benzodixanthene into the parent hydrocarbon and oxygen is shown to be an adiabatic photoreaction originating from an upper excited singlet state. This photochemical behaviour is described by a theory for the photochemistry of endoperoxides developed by Kearns and Khan.

Introduction

In 1969 Kearns and Khan derived a state correlation diagram describing the formation and the cleavage of the endoperoxide of cyclopentadiene [1]. As the authors pointed out, the following two predictions concerning the photochemistry of this endoperoxide should also generally be valid for endoperoxides of aromatic compounds:

1. excitation of the S_1 - and T_1 -state should cause a homolytic splitting of the peroxide bridge,
2. excitation of an upper singlet state should lead to an adiabatic cleavage into singlet oxygen and parent hydrocarbon in its ground state.

Thus the photochemistry of endoperoxides should exhibit some outstanding aspects:

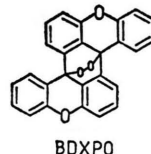
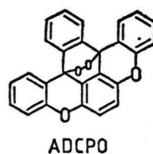
1. the existence of two different reaction channels,
2. the possibility of reversible photochemistry, i.e. photochromism and
3. a new type of photoreaction in solution combining both rare cases of an adiabatic photoreaction and a reaction originating from an upper excited singlet state, i.e. wavelength dependent photochemistry.

For the first time we could confirm these predictions for the endoperoxides of heterocordianthrone (HCDPO) and of 9,10-diphenylanthracene (DPAPO) [2, 3].

For the endoperoxide of rubrene (RUBPO), we found a likewise wavelength dependent quantum yield Q_1 for the cleavage into oxygen and rubene,

indicating that the reaction originates from an upper excited singlet state. But in this case the quantum yield Q_{dec} for the rearrangement reaction, which follows the homolytic splitting of the peroxide bridge, was much larger than Q_1 . Hence for RUBPO we could not examine whether the photocleavage occurs adiabatically or not [4].

In the meantime we found some structural characteristics for endoperoxides which diminish the quantum yield Q_{dec} [5]. Following this concept we synthesized the endoperoxides of anthra[1,9-bc; 4,10-b'c']dichromen (ADCPO) and benzo[1,2,3-kl; 4,5,6-k'l']dixanthen (BDXPO), which are highly reversible photochromic compounds. Since Q_1 is much larger than Q_{dec} for both endoperoxides, both



compounds are especially suitable for an investigation of the photocleavage into parent hydrocarbon and oxygen. In order to prove if this photoreaction also belongs to the new type of reaction, we studied the photochemistry of ADCPO and BDXPO in detail.

Experimental

ADCPO and BDXPO were prepared and purified as previously described [5]. 1,3-Diphenylisobenzofuran from EGA was recrystallized twice from ethanol. Toluene (MERCK, spectroscopic grade) was used without further purification.

The absorption spectra were recorded on a Perkin-Elmer PE 555 spectrophotometer. The ap-

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paratus for the determination of the photochemical quantum yields is described in detail in an earlier paper [6]. All experiments were run at room temperature.

Results and Discussion

The absorption spectra of anthradichromene (ADC) and ADCPO, and of benzodixanthene (BDX) and BDXPO are shown in Figs. 1 and 2, respectively. As one can see from these, the absorption of the hydrocarbons shifts by more than 200 nm to the uv upon photooxidation. ADCPO and BDXPO have their first absorption maximum above 30000 cm^{-1} . The extinction coefficient of both endoperoxides decreases with increasing wavelength, showing a slight shoulder in each case.

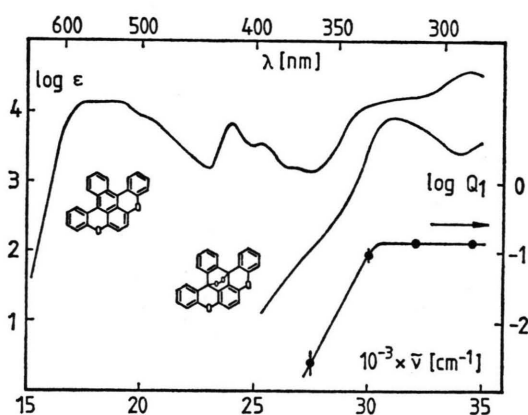


Fig. 1. Absorption spectra of ADC and ADCPO, wavelength dependence of Q_1 , solvent toluene.

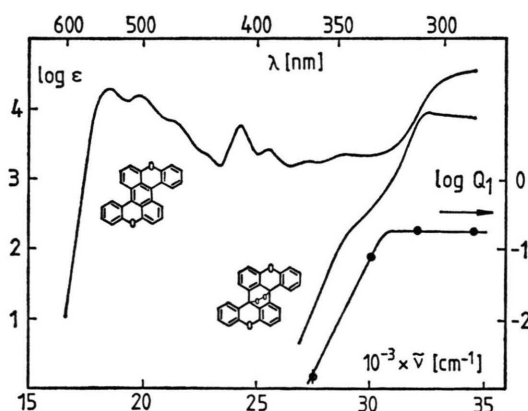


Fig. 2. Absorption spectra of BDX and BDXPO, wavelength dependence of Q_1 , solvent toluene.

The quantum yield Q_1 for the cleavage of the endoperoxides into parent hydrocarbon and oxygen is given in Figs. 1 and 2 as a function of wavelength on a logarithmic scale. In order to determine Q_1 the formation of the hydrocarbons was monitored spectrophotometrically. Since the produced hydrocarbons absorb stronger at the irradiation wavelengths than the endoperoxides, the photolysis was terminated after 1 percent conversion and, when necessary, corrected for the absorption of the products.

The wavelength dependence of Q_1 , which we observed for both endoperoxides, is a similar one as we found for HCDPO, DPAPO and RUBPO. Q_1 has a constant value in the high energy absorption region but falls off sharply upon irradiation in the long wavelength region of the absorption.

For ADCPO we determined Q_1 for irradiation at 290 and 313 nm to be 0.13, but at 365 nm to be only 0.0026. For BDXPO one gets an even stronger decrease in Q_1 from 0.18 at 290 and 313 nm to only 0.0015 at 365 nm.

From this it follows that the S_1 -state or a hot ground state cannot be the initial state of the photocleavage. Although we did not perform additional sensitized photolysis experiments and experiments with heavy atom substituted derivatives, as in the case of the very detailed study of HCDPO [2], we conclude from the analogy in the wavelength dependence of HCDPO and both new endoperoxides that this photoreaction originates from an upper excited singlet state S_n , $n \geq 2$.

This result agrees in part with the mechanism postulated by Kearns and Khan. The second part of the prediction concerning the photocleavage, is the hypothesis that this photoreaction occurs adiabatically under formation of singlet oxygen. In order to prove this we performed trapping experiments during the photolysis of the endoperoxides. 1,3-Diphenylisobenzofuran (DPI) reacts very rapidly with $O_2(^1\Delta_g)$ ($k_{DPI} = 7 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ [7]), and is, therefore, especially suitable as singlet oxygen scavenger [8].

We irradiated, by six thaw and freeze cycles at 10^{-6} bar carefully degassed mixed solutions of endoperoxide and DPI in toluene at 313 nm. Under these conditions selfsensitized photooxidation of DPI is negligible and the spectrophotometrically determined consumption of DPI is only due to the reaction with $O_2(^1\Delta_g)$, produced during the photo-

lysis of the endoperoxides. Since O_2 and hydrocarbon (HC) are formed in equal amounts, the spectrophotometrically determined increase in $[HC]$ monitors the production of O_2 .

The hydrocarbons originating during the irradiation react with $O_2(^1\Delta_g)$ with a smaller rate constant than DPI: $k_{ADC} = 5.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{BDX} = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [9]. Since the mean concentrations $[HC]$ during the experiments are about one order of magnitude smaller than $[DPI]$, $O_2(^1\Delta_g)$ formed during the photolysis is mainly consumed by reaction with DPI and by physical deactivation with rate constant k_{DEA} . Using the photostationary state approximation one obtains

$$\alpha \frac{d[HC]}{dt} = (k_{DEA} + k_{DPI}[DPI])[^1O_2], \quad (1)$$

where α is the yield of 1O_2 with respect to the total amount of produced HC.

The reaction of DPI follows a second order rate law:

$$-\frac{d[DPI]}{dt} = k_{DPI}[DPI][^1O_2]. \quad (2)$$

From (2) one approximates for the photostationary concentration of $[^1O_2]$:

$$[^1O_2] \approx -\frac{1}{k_{DPI}} \frac{d \ln [DPI]}{dt}. \quad (3)$$

Combination of (3) and (1) results in

$$\alpha \approx -\frac{d \ln [DPI]}{d[HC]} \left(\frac{k_{DEA}}{k_{DPI}} + [DPI] \right). \quad (4)$$

Plots of $\ln [DPI]$ versus $[HC]$, which are presented in Fig. 3, exhibit the linear correlation expected from equation (4). With $k_{DEA} = 5 \times 10^4 \text{ s}^{-1}$ [7], the experimentally determined slopes, and the values for $[DPI]$ (see Fig. 3) one obtains yields of 1O_2 of

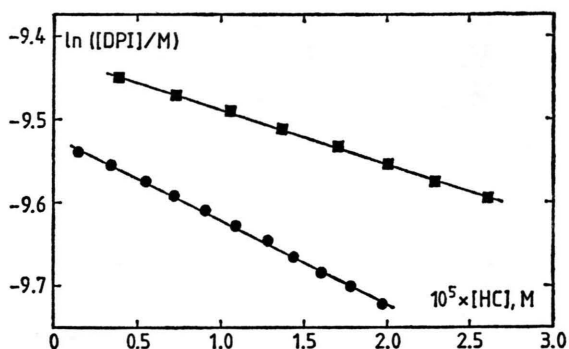


Fig. 3. Singlet oxygen trapping experiments, ● ADC, ■ BD, solvent toluene.

$\alpha = 1.1 \pm 0.3$ for ADCPO and $\alpha = 0.9 \pm 0.3$ for BDXPO.

These values establish that 1O_2 and HC are formed in equal amounts during the photocleavage of both endoperoxides. Whether the excited oxygen is primarily generated as very short lived $O_2(^1\Sigma_g^+)$, as expected by the theory, can of course not be decided, since only the relatively long lived $O_2(^1\Delta_g)$ can be trapped.

From our work it follows that ADCPO and BDXPO are two further rare examples of endoperoxides which exhibit the new reaction type of an adiabatic photoreaction originating from an upper excited singlet state. To determine whether the theoretical description of the photochemistry of endoperoxides given by Kearns and Khan is generally valid, we will do more quantitative work in this field of interest.

Acknowledgement

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