The Endoperoxide of Tetrabenzopentancene. A New Photochromic Endoperoxide

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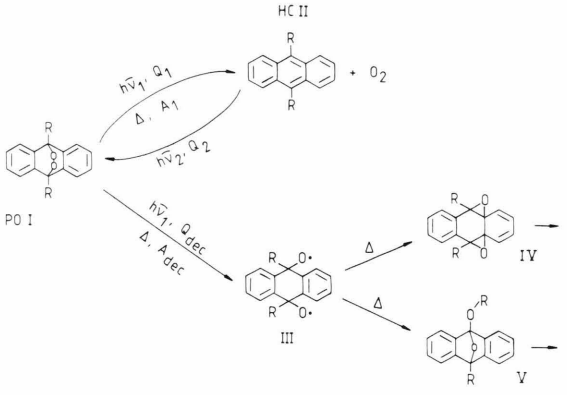
The thermal and the photochemical reactions of the endoperoxide of Tetrabenzo(bc,fg,lm,pq)-pentacene have been investigated with respect to its photochromic properties. The thermal yield of irreversible rearrangement reactions was determined to be $A_{dec} = 0.045$. From the activation parameters of the thermal cycloreversion, forming the parent hydrocarbon and oxygen, a half life time of 114 years at 20 °C has been extrapolated. For the quantum yield of the irreversible photochemical rearrangement a value of $Q_{dec} = 0.03$ was obtained. As can be seen from the wavelength dependence of the photocycloreversion quantum yield Q_1, cycloreversion occurs not only from the thermalized $S_2(\pi_{cc}\pi^*_{cc})$ but from higher excited states too. The maximum quantum yield was found at 302 nm to be $Q_1 = 0.15$. From our results it follows that this endoperoxide is of high quality in respect to the colour change colourless/blue and to thermal stability, whereas the reversibility is only moderate.

Introduction

Endoperoxides (POs) of aromatic hydrocarbons (HCs) are known to undergo the same two competing reactions in thermal chemistry and in photochemistry. The cycloversion of PO may be induced by heat as well as by uv irradiation and leads to the regeneration of the parent HC and O_2 with the thermal yield A_1 and the quantum yield Q_1, respectively [1–4]. Since this reaction is the reversal of the photooxidative formation of PO, which



occurs with quantum yield Q_2, systems PO/HC + O_2 are in principal photochromic [5]. The degree of reversibility, however, is limited by the extent of the competing irreversible rearrangement reactions of PO, proceeding in the first step via the intermediate biradical III.

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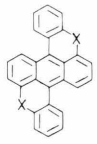
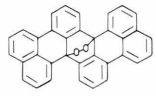
The homolytic rupture of the peroxide bridge may be achieved again thermally or photochemically, the yields of the irreversible rearrangement being A_{dec} and Q_{dec}, respectively [6, 7]. The quantum yield Q_{dec} depends on the molecular structure of PO and values of $0.004 \leqq Q_{dec} \leqq 0.8$ have already been found [2, 3]. Since the ratio Q_1/Q_{dec} is a quantitative measure for the reversibility of a photochromic PO, it is of main importance to reduce Q_{dec} in order to get photochromic materials of high reversibility.

In a preceeding publication we have demonstrated the existence of a close correlation between A_{dec} and Q_{dec}. Basing on this and on literature data we proposed a concept for the molecular structure of POs with low tendency towards rearrangement [8]. Following our concept a PO should have low Q_{dec} and A_{dec} values if it is derived from a 9,10-diphenylanthracene in which the phenyl substituents are additionally fixed by bridges X to the anthracene frame as, for example, in formula VI. This kind of sterical arrangement hinders the formation of the diepoxide IV and of the cyclic ether V, which are the main intermediate products on the rearrangement route [6–8].



VI

TBP VII



TBPPO VIII

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The bridging groups X = O and X = CO lead to highly reversible photochromic POs [5, 8, 9]. In order to test if a different fixation of the phenyl substituents to the anthracene moiety will also result in good photochromic properties we decided to investigate the photooxidation product of HC VII. This compound was first synthesized and characterized by Clar et al. as 1,9,5,10-diperinaphthylene-anthracene and has now to be called tetrabenzo(bc, fg,lm,pq)pentacene (TBP) [10].

Nothing was reported about the photooxidational behaviour of TBP but Clar mentioned that TBP adds readily maleic anhydride [10]. Because of the strong correlation between photooxidation and maleic anhydride addition of aromatic compounds, however, we expected TBP to be photooxidizable and to form the endoperoxide TBPPO VIII, which we hoped to be a highly reversible photochromic compound.

Experimental

Toluene from the Uvasol series of Merck was used as solvent for the spectroscopic and most photochemical measurements. All other solvents were of analysis grade from Merck.

TBP was prepared following the procedure described by Clar et al. [10]. For the purification of the product column chromatography (silica gel, dichloromethane/benzene 3/2) was applied. However, the first fraction, which was deep blue coloured, turned out to be a composite of the blue TBP (main product) and a blue violet contamination ($\lambda_{max} = 594$ nm). After evaporation of the solvent the mixture was dissolved in a small amount of oxygen saturated carbondisulfide and irradiated with filtered sun light (cut off: 450 nm). Surprisingly the dark blue solution was readily decolourized, i.e. both components form colourless POs. Fortunately the POs proved to be of strikingly different thermal stability. Therefore the PO mixture was dissolved in toluene and heated for 5 min to 100 °C (half life time $\tau_{1/2}$ of the contamination-PO = 30 s, $\tau_{1/2}$ of TBPPO = 3.3 h). By this procedure 99.9% of the contamination-PO and only 2% of TBPPO were thermolyzed, producing the parent HCs. Afterwards this mixture could be separated easily by column chromatography (silica gel, toluene), TBPPO being the second fraction. TBP was obtained by thermolysis of pure TBPPO at 130 °C in m-xylene ($\tau_{1/2} = 310$ s) and subsequent chromatography (silica gel, xylene). In the following the maxima of absorption (nm; log ε) of TBP and TBPPO are given, which may be compared with Clars results for TBP and benzanthrene: TBP, toluene: (627; 4.62), (578; 4.36), (413; 3.28), (292; 4.59). TBPPO, toluene: (347; 4.52), (330; 4.50), (317; 4.33). TBP, benzene [10]: (630; 4.64), (579; 4.40), (412; 3.47), (292; 4.76). benzanthrene, alcohol [10]: (344; 4.14), (329; 4.22), (312; 4.08).

Electronic spectra were recorded on a PE 555 spectrophotometer of Perkin-Elmer. The apparatus for the determination of the quantum yields is described in detail in an earlier publication [11]. For the determination of Q_{dec} the irreversible consumption of TBPPO was measured by HPLC.

Results and Discussion

Spectra

The electronic spectra of TBP and TBPPO are shown in Figure 1. Obviously a very large spectral shift of 280 nm accompanies the photooxidation of TBP. The structural formula VIII proposed for TBPPO is confirmed by the absorption spectrum, which matches very well with the long wave maxima of benzanthrene, being the $\pi_{cc}\,\pi^*_{cc}$ chromophore of structure VIII. This can be seen from a comparison of the respective maxima listed in the experimental section. Since two benzanthrene chromophores are found in TBPPO, the extinction coefficients of the maxima are about twice as great for TBPPO than for benzanthrene. The transition of the peroxide chromophore of aromatic compounds usually requires about 23 000 cm^{-1} [3, 12]. However, at this wavenumber the extinction coefficient of the corresponding absorption band amounts to only $\varepsilon \leqq 1\ M^{-1}\,cm^{-1}$. This is about four to five orders of magnitude smaller than the extinction coefficient of the very strong $S_2\,(\pi_{cc}\,\pi^*_{cc})$ band lying at 28 800 cm^{-1}. That is why for TBPPO the $S_1\,(\pi^*_{00}\,\delta^*_{00})$ band can not be discerned spectrophotometrically.

benzanthrene

Thermolysis

Generally in thermal PO chemistry cycloreversion has to compete with rearrangement, the latter being

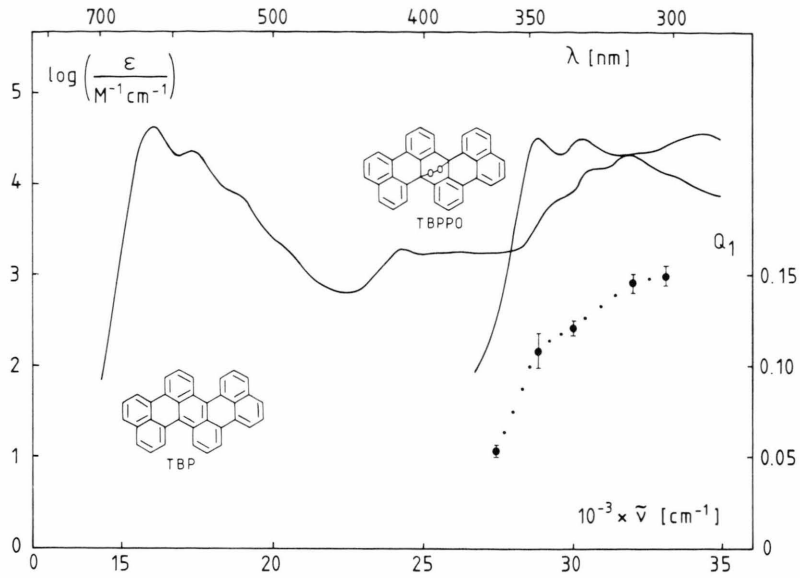

Fig. 1. Electronic spectra of TBP and TBPPO in toluene. ● = experimental values of Q_1 with error bar, in toluene.

sensitive to sterical restrictions [8]. A first test to see whether the new kind of aromatic fixation of the phenyl substituents to the anthracene frame of the PO is suited to reduce the tendency towards rearrangement is the determination of A_{dec}, the yield of irreversibly rearranged products during total PO thermolysis.

For that purpose the concentration of a TBP solution in m-xylene was determined spectrophotometrically. Afterwards the solution was photooxidized completely using sun light and a 450 nm cut off filter. The oxygen was then removed from the solution by bubbling a stream of nitrogen being saturated with m-xylene vapor. Subsequently the solution was boiled in the dark under reflux (139 °C). Each 5 min a sample was taken for spectrophotometric analysis. 15 min (i.e. about $5 * \tau_{1/2}$) after the beginning a maximum in the TBP absorption was reached. Further boiling led to a very slow degradation of TBP. From an extrapolation of the absorbance at 627 nm to the starting time of heating the maximum concentration of TBP was obtained, which could be got by cycloreversion if degradation of TBP would not occur. The ratio of this concentration and the concentration of TBP before photooxidation is the thermal yield of cycloreversion A_1, amounting to 0.955 ± 0.005. Therefore the yield of rearranged products is $A_{dec} = 0.045 \pm 0.005$.

For the determination of the activation parameters of the thermal cycloreversion TBPPO solutions were thermolized in the way described above. The formation of TBP was followed spectrophotometrically for at least two half life times. Table 1 lists the cycloversion rate constants, from which the activation energy $E_a = 34.5$ kcal/mole and the logarithm of the A-factor $\log A = 16.0$ can be calculated. From these data the half life time of TBPPO in respect to cycloreversion is extrapolated to be 114 years. Therefore TBPPO belongs to the exceptional stable POs.

Photolysis

Cycloreversion and rearrangement reactions take place in photochemistry of POs too. Excitation of the $S_1(\pi^*_{00}\delta^*_{00})$ state, localized on the peroxide chromophore, exclusively yields rearranged products [3, 6]. Irradiation of the $\pi_{cc}\pi^*_{cc}$ bands leads to cleavage of PO under formation of HC and O_2 [2–4, 13]. Since internal conversion from the $S_n(n \geqq 2)\,\pi_{cc}\pi^*_{cc}$ states, which leads ultimately to

Table 1. Cycloreversion rate constants k for TBPPO in O_2-free m-xylene; error in $k \pm 3\%$, in $T \pm 0.5$ K.

T[K]	372.7	384.2	402.2	404.7
k[s^{-1}]	$5.87 \cdot 10^{-5}$	$2.40 \cdot 10^{-4}$	$1.75 \cdot 10^{-3}$	$2.33 \cdot 10^{-3}$

$S_1(\pi^*_{00}\delta^*_{00})$, competes effectively with cycloreversion, rearrangement always accompanies photocycloreversion.

The cycloreversion quantum yield Q_1 is given on a linear scale in Fig. 1 for five irradiation wavelengths. Q_1 has a maximum value of 0.149 ± 0.007 and is almost wavelength independent only between 302 and 313 nm. Q_1 decreases already in the range of the $\pi_{cc}\pi^*_{cc}$ bands to a value of 0.11 at the first maximum of absorption of TBPPO. Therefore cycloreversion does not only take place from the thermalized $S_2(\pi_{cc}\pi^*_{cc})$ state but also from higher electronically or/and vibrationally excited states. A similar behaviour has already been found by us for the POs of the tetracene series [4]. In the overlapping region S_2/S_1 a further decrease in Q_1 is observed, as is usually found for POs.

Two different methods have been applied for the determination of the quantum yield of rearrangement Q_{dec}. In the first experiment an O_2-free TBPPO solution in m-xylene was irradiated at 365 nm until a total conversion of TBPPO of 45% was achieved. Under these conditions the number of light quanta absorbed by TBPPO can only be evaluated by simultaneously measuring the photolytically formed TBP as an internal standard ($Q_1(365)$ in m-xylene = 0.055). If Δ[TBP] and Δ[TBPPO] − Δ[TBP] are the reversible and the irreversible conversions of TBPPO in concentration units, one has

$$Q_{dec}(365) = Q_1(365) * (\Delta[\text{TBPPO}] - \Delta[\text{TBP}])/\Delta[\text{TBP}]\,. \quad (1)$$

The total conversion Δ[TBPPO] was measured by HPLC, the reversible conversion of TBPPO, Δ[TBP], was determined spectrophotometrically. In this way a value $Q_{dec}(365) = 0.034 \pm 0.006$ was obtained.

Since the system TBPPO/TBP + O_2 is photoreversible, uv irradiation of an air saturated TBPPO solution always leads to an equilibrium state. Because the rearrangement reactions of TBPPO accompany cycloreversion, a consumption of TBPPO and TBP during prolonged irradiation is expected. Actually the TBP absorbance decreases slowly and for moderate conversions linearly after having reached the equilibrium value. If one assumes that irreversible photochemical side reactions only take place from the PO, Q_{dec} can be calculated from the disappearance of the HC absorbance in the equilibrium, as is described in detail in [8]. From this experiment a value $Q_{dec}(365) = 0.028 \pm 0.006$ was calculated. Thus the mean value determined by two different methods is $Q_{dec}(365) = 0.03 \pm 0.006$ in m-xylene.

The approximately equal values obtained for A_{dec} and Q_{dec} are in accordance with the close correlation between A_{dec} and Q_{dec} found for a series of POs [8, 14]. This correlation results from the fact that both the photochemical and the thermal rearrangement of POs proceed via the same intermediate, which is produced by homolytic rupture of the peroxide bridge [6–8]. If the subsequent rearrangement of the biradical is sterically hindered, reformation of ground state PO gains more importance and A_{dec} and Q_{dec} will be reduced in similar amounts.

Q_{dec} is significantly smaller for TBPPO than for the endoperoxide of 9,10-diphenylanthracene (Q_{dec} = 0.075 [15]). Apparently the aromatic fixation of the phenyl substituents to the anthracene frame has the desired effect and reduces Q_{dec} by a factor of 2.5. However, the aromatic fixation is of only minor quality in respect to the prevention of the rearrangement reactions if it is compared with the fixation by ether or keto bridges (X = O, CO in formula VI). This is demonstrated by a comparison of the Q_{dec} values which are about three times smaller for photochromic POs with X = O and five times smaller for PLOs with X = CO [3, 8, 9].

Photochromic properties

The system TBPPO/TBP + O_2 is a photoreversible photochromic system of medium quality. It is distinguished by the largest spectral shift found so far for POs, which even leads to a colour change colourless/blue. Furthermore TBPPO is of extraordinary high thermal stability ($\tau_{1/2}$ = 114 years at 20 °C). This is a great advantage because of the uncomplicated handling and storing of the photochromic material, which can be done at ambient temperature.

However, the reversibility is of less good quality. This is caused by the combination of the relatively high Q_{dec} value with the rather small maximum value of $Q_1 = 0.15$, which lies at the lower margin of the Q_1 values found for other photochromic POs ($0.13 \leqq Q_1 \leqq 0.58$). A measure for the reversibility is the number n of photochromic cycles up to which

a PO is degraded to $1/e$ of the starting concentration. n is approximately given by

$$n = Q_1/(Q_{dec}\, U) \qquad (2)$$

with U the conversion of PO per cycle [5]. If one assumes $U = 0.05$ for the colouring reaction (photocycloreversion) and subsequent complete decolourization by photooxidation one obtains for TBPPO

$$n = 0.15/(0.03 * 0.05) = 100\,.$$

Thus, compared with the ether and keto bridged photochromic POs, the reversibility of TBPPO is smaller by factors of 2.5–3.5 and 10–30, respectively.

Acknowledgement

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