

## COMPARISON OF THE PHOTOCHEMICAL AND THERMAL REARRANGEMENT REACTION OF ENDOPEROXIDES

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### Summary

The yields  $Q_{\text{dec}}(S_1)$  and  $A_{\text{dec}}$  of the photochemical and thermal rearrangement reaction have been determined for 13 endoperoxides of the anthracene and tetracene series. A strong substituent effect operates on  $Q_{\text{dec}}(S_1)$  and  $A_{\text{dec}}$ , which are closely correlated. The interpretation of our results leads to the postulate that the lowest excited singlet state of endoperoxides is deactivated exclusively by a chemical process, by O—O bond breakage on the repulsive  $S_1$  potential surface. Re-formation of ground state endoperoxide occurs by subsequent O—O bond formation. This conclusion is confirmed by the observation that even for photochromic endoperoxides with low  $Q_{\text{dec}}(S_1)$  neither fluorescence nor phosphorescence occur.

The intermediate biradical, which is the common precursor in the photochemical and thermal rearrangements, is involved in a chemical equilibrium with ground state endoperoxide. For the photochromic endoperoxides, and most other endoperoxides, the rate constants of thermal cycloreversion and of thermal O—O bond cleavage are of the same order of magnitude.

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### 1. Introduction

It is known that endoperoxides of aromatic hydrocarbons undergo the same two reactions in their photochemistry as in their thermal chemistry. The reversible reaction is a cycloreversion which re-produces the parent hydrocarbon and oxygen ( $^3O_2/{}^1O_2$ ) with a quantum yield  $Q_c$  and a thermal yield  $A_c$  [1 - 5]. The irreversible reaction is a rearrangement which is initiated by the homolytic rupture of the O—O bond, forming a biradical as the first intermediate. This was elucidated by Rigaudy and coworkers in a number of carefully carried out investigations on some endoperoxides of the anthracene and tetracene series [6 - 8]. They found out that thermally and photochemically the same rearranged products are formed, all having the biradical as a common precursor [9, 10].

For a lot of endoperoxides of anthracene derivatives the  $A_c$  have been determined previously [11], revealing a strong substituent effect on  $A_c$  and

consequently on  $A_{dec}$ , which is defined as the thermal yield of all rearranged products:

$$A_{dec} = 1 - A_c \quad (1)$$

We concluded that the substituent effect operating on  $A_{dec}$  should work in the same way on the quantum yield  $Q_{dec}(S_1)$  of the rearrangement reaction upon  $S_1$  excitation if the photochemical and thermal rearrangement proceed via the same biradical intermediate. In our search for photochromic systems we therefore investigated the photochemical rearrangement of several endoperoxides. In fact a good correlation between  $A_{dec}$  and  $Q_{dec}(S_1)$  was observed, which prompted us to deduce successfully the particular structural characteristics that enable endoperoxides to act as components of highly reversible photochromic systems [12, 13].

In the meantime, we have investigated a larger number of endoperoxides with respect to their thermal and photochemical rearrangement reaction. Thus more experimental data are available for a comparison of these reactions.

## 2. Experimental details

All endoperoxides investigated were prepared by sensitized or self-sensitized photo-oxidation of the parent aromatic hydrocarbon. Detailed information on the synthesis and purification is given for the endoperoxides of anthracene (APO) and 9,10-dimethylantracene (DMAPO) in ref. 14, for the endoperoxide of 9,10-diphenylantracene (DPAPO) in ref. 2, for the endoperoxide of 1,4,9,10-tetraphenylantracene (TPAPO) in ref. 15, for the endoperoxides of tetracene (TPO), 5,12-diphenyltetracene (DPTPO) and rubrene (RUBPO) in ref. 16, for the endoperoxide of tetrabenzopentacene (TBPPO) in ref. 17, for the endoperoxides of anthradichromene (ADCPO) and benzodixanthene (BDXPO) in ref. 12, for the endoperoxide of dimethyl-homocoerdianthrone (HOCDPO) in ref. 18 and for the endoperoxide of heterocoerdianthrone (HECDPO) in ref. 19.

Sensitized photo-oxidation of benzoterrylene (BT), which was prepared according to Clar *et al.* [20], gave the corresponding endoperoxide (BTPO). The synthesis was carried out in oxygen-saturated carbon disulphide with polymer-bound Rose Bengal as the sensitizer, using sunlight and a 450 nm cut-off filter. After filtration and evaporation of the solvent the product was purified by column chromatography (silica gel, 60vol.%toluene-40vol.%-dichloromethane). BTPO was identified by a comparison of its absorption maxima with the respective maxima of the structure analogue disodium salt from the maleic anhydride adduct (BTMAA) of BT. (BTPO, dichloromethane: 383, 4.56; 362, 4.54; 344, 4.30. BTMAA, alcohol: 388, 4.84; 367, 4.78; 348, 4.50; see ref. 20.) All manipulations of endoperoxides were carried out under red light in order to prevent degradation.

The solvents used were toluene (TOL) and dichloromethane (DCM) (both Uvasol, Merck) and *m*-xylene (XYL) (analysis grade, Merck).

Electronic spectra were recorded using a PE 555 spectrophotometer from Perkin-Elmer. Luminescence measurements were performed in a home-built instrument described previously [21]. The apparatus for the determination of the quantum yields is described in detail in ref. 22. The high performance liquid chromatography (HPLC) measurements were performed using a 3B device from Perkin-Elmer.

For the determination of  $A_c$ , endoperoxide solutions of starting concentrations  $[PO]_0$  in XYL were deoxygenated by bubbling through a stream of nitrogen that was saturated with XYL vapour. Subsequently, the solutions were boiled in the dark under reflux (139 °C). After suitable time intervals, samples were taken for the spectrophotometric determination of the HC concentration. The ratio of the maximum concentration  $[HC]_{max}$  to  $[PO]_0$  gave the thermal yield of cycloreversion  $A_c$ .  $A_{dec}$  was calculated according to eqn. (1).

For the evaluation of the quantum yield  $Q_{dec}(\lambda)$  of rearrangement at the irradiation wavelength  $\lambda$ , both the irreversible consumed endoperoxide and the number  $N(\lambda)$  of photons absorbed by the endoperoxide have to be known. If  $\Delta[HC]$  is the reversible conversion of endoperoxide and  $\Delta[PO]$  is the entire conversion of endoperoxide, then the difference  $\Delta[PO] - \Delta[HC]$  represents the irreversibly consumed endoperoxide during irradiation, and

$$Q_{dec}(\lambda) = \frac{(\Delta[PO] - \Delta[HC])V}{N(\lambda)} \quad (2)$$

where  $V$  is the sample volume.

$\Delta[HC]$  was always determined spectrophotometrically. Since at the end of each experiment the endoperoxide absorption is always superposed by the absorption of photolysis products, direct spectrophotometric measurement of  $\Delta[PO]$  is therefore impossible. The following three different methods have been used for the determination of  $\Delta[PO]$ .

(a) For endoperoxides with large values of  $A_c$ ,  $\Delta[PO]$  was obtained indirectly by spectrophotometric analysis. Irradiated (i) and unirradiated (u) solutions of equal initial concentration  $[PO]_0$  were thermolysed as described above. Using the values of  $[HC(i)]_{max}$ ,  $\Delta[PO]$  was calculated from the equation

$$\Delta[PO] = \frac{([HC(u)]_{max} - [HC(i)]_{max})[PO]_0}{[HC(u)]_{max}} \quad (3)$$

(b)  $[PO]$  was determined directly by quantitative HPLC analysis.

(c) For endoperoxides with small values of  $Q_{dec}(\lambda)$ , endoperoxide/hydrocarbon +  $O_2$  systems are photoreversible, and prolonged UV irradiation of an air-saturated endoperoxide solution always leads to a photochemical equilibrium. However, owing to the irreversible rearrangement, the hydrocarbon absorbance does not remain constant in the equilibrium state but decreases slowly and for moderate conversions almost linearly.  $\Delta[PO]$  can be calculated from the disappearance of the HC absorbance, as is described in detail in ref. 12.

The determination of  $N(\lambda)$  requires some effort because of the developing inner-filter effect. Two methods have been applied to estimate  $N(\lambda)$ .

(1) By measurement of the absorbance at  $\lambda$  at the beginning and at the end of the experiment and considering  $\Delta[\text{PO}]$  (see above), the mean inner filter can be calculated. The quantum flux of the irradiation beam was measured using a calibrated photodiode and thus  $N(\lambda)$  was determined.

(2) A different method was used in experiments with large endoperoxide conversions. This internal-standard method requires the knowledge of the cycloreversion quantum yield  $Q_c(\lambda)$  at  $\lambda$ .  $N(\lambda)$  may then be calculated from  $Q_c(\lambda)$  and  $\Delta[\text{HC}]$  using the equation

$$Q_c(\lambda) = \frac{\Delta[\text{HC}]V}{N(\lambda)} \quad (4)$$

that defines  $Q_c(\lambda)$ . Insertion of  $N(\lambda)$  into eqn. (2) yields

$$Q_{\text{dec}}(\lambda) = \frac{(\Delta[\text{PO}] - \Delta[\text{HC}])Q_c(\lambda)}{\Delta[\text{HC}]} \quad (5)$$

Thus the  $Q_{\text{dec}}(\lambda)$  were determined by method a1 (method (a) for  $\Delta[\text{PO}]$  in conjunction with method (1) for  $N(\lambda)$ ) and/or a2, b1, b2, c. All photochemical experiments were performed at room temperature and, with the exception of those following method c, all were carried out in oxygen-free solutions.

### 3. Results

The values of  $A_c$  for a large number of endoperoxides are summarized in ref. 11. However, as these values were determined at different temperatures by heating solid endoperoxide samples, they are not very suitable for means of comparison. Therefore we determined the values of  $A_c$  for each of the investigated endoperoxides in solution at 139 °C, regardless of whether literature values already existed or not. From these  $A_c$  the  $A_{\text{dec}}$  were calculated according to eqn. (1).

The  $Q_{\text{dec}}(\lambda)$  depend on the irradiation wavelength, since photochemical rearrangement occurs exclusively upon excitation of the  $S_1$  state of the endoperoxides. Upon irradiation with light of shorter wavelength, photocycloreversion takes place with a quantum yield  $Q_c(\lambda)$ , and this process competes with internal conversion (IC) to  $S_1$  which occurs with a quantum yield  $1 - Q_c(\lambda)$ . Therefore  $Q_{\text{dec}}(\lambda)$  is reduced to

$$Q_{\text{dec}}(\lambda) = \{1 - Q_c(\lambda)\}Q_{\text{dec}}(S_1) \quad (6)$$

Equation (6) describes satisfactorily the experimentally found wavelength dependence of  $Q_{\text{dec}}(\lambda_1)$  [1]. It may therefore be used to calculate the  $Q_{\text{dec}}(S_1)$  values for those endoperoxides for which the direct determination could not be performed because of the very low extinction coefficients ( $\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$ ) for the respective  $S_1$  bands [14].

TABLE 1

Thermal and photochemical yields of rearrangement of endoperoxides

<i>Endo-peroxide</i>	$A_{dec}^a$	$Q_{dec}(\lambda)$	$\lambda$ (nm)	$Q_c(\lambda)$	$Q_{dec}(S_1)$	<i>Solvent</i>
APO	$0.99 \pm 0.003$	$0.75 \pm 0.08^b$	270	0.22	$0.96 \pm 0.1$	DCM
DMAPO	$0.46 \pm 0.05$	$0.22 \pm 0.03^b$	270	0.35	$0.34 \pm 0.05$	DCM
DPAPO	$0.06 \pm 0.015$		330		$0.075 \pm 0.015^c$	TOL
TPAPO	$0.06 \pm 0.015$	$0.13 \pm 0.02^b$	302	0.091	$0.13 \pm 0.02^d$	XYL
		$0.11 \pm 0.03^e$	302			
TPO	$> 0.995$	$0.9 \pm 0.1^b$	248	0.055	$0.95 \pm 0.1$	DCM
DPTPO	$0.60 \pm 0.03$	$0.24 \pm 0.03^b$	248	0.073	$0.26 \pm 0.03$	DCM
RUBPO	$0.25 \pm 0.03$	$0.20 \pm 0.03^e$	313	0.013	$0.20 \pm 0.02^d$	XYL
		$0.20 \pm 0.03^e$	365			
BTPO	$0.03 \pm 0.01$	$0.03 \pm 0.01^b$	365	0.087	$0.033 \pm 0.01$	TOL
TBPPO	$0.05 \pm 0.015$	$0.028 \pm 0.004^f$	365	0.055	$0.033 \pm 0.003^d$	XYL
		$0.034 \pm 0.005^b$	365			
ADCPO	$0.01 \pm 0.005$	$0.010 \pm 0.002^f$	313	0.13	$0.011 \pm 0.002$	TOL
BDXPO	$0.01 \pm 0.005$	$0.010 \pm 0.002^f$	313	0.18	$0.012 \pm 0.002$	TOL
HOCDPO	$0.015 \pm 0.005$	$0.0085 \pm 0.0015^c$	390	0.1 <sup>g</sup>	$0.010 \pm 0.002$	TOL
HECDPO	$< 0.005$	$0.0058 \pm 0.0006^c$	388	$7 \times 10^{-4}$	$0.006 \pm 0.0006^d$	TOL
		$0.0045 \pm 0.001^f$	313			

<sup>a</sup>In boiling XYL (139 °C).<sup>b</sup>Method b2 (as described in Section 2).<sup>c</sup>Method a1.<sup>d</sup>Mean of values obtained by different methods.<sup>e</sup>Method a2.<sup>f</sup>Method c.<sup>g</sup>Interpolated value.

Table 1 lists the experimental data together with the calculated values for  $Q_{dec}(S_1)$ . The structures of the investigated endoperoxides are given in Fig. 1; they are drawn in such a way that they reveal the common chemical behaviour of the endoperoxides (not following the IUPAC nomenclature).

## 4. Discussion

### 4.1. Kinetic schemes

The question arises of how to understand the strong substituent effect on  $Q_{dec}(S_1)$ . The results of Rigaudy *et al.* clearly reveal that in the initial step of the thermal and of the photochemical rearrangement of endoperoxides homolytic O—O bond cleavage occurs. The biradical intermediate rearranges to form mainly a diepoxide as the primary product, and this is stabilized by further subsequent rearrangement [6 - 10].

The unsubstituted endoperoxides APO and TPO have the maximum possible values  $Q_{dec}(S_1) = 1$ .  $Q_{dec}(S_1)$  decreases if the carbon atoms next to the peroxide bridge are bound to space-demanding groups such as methyl or

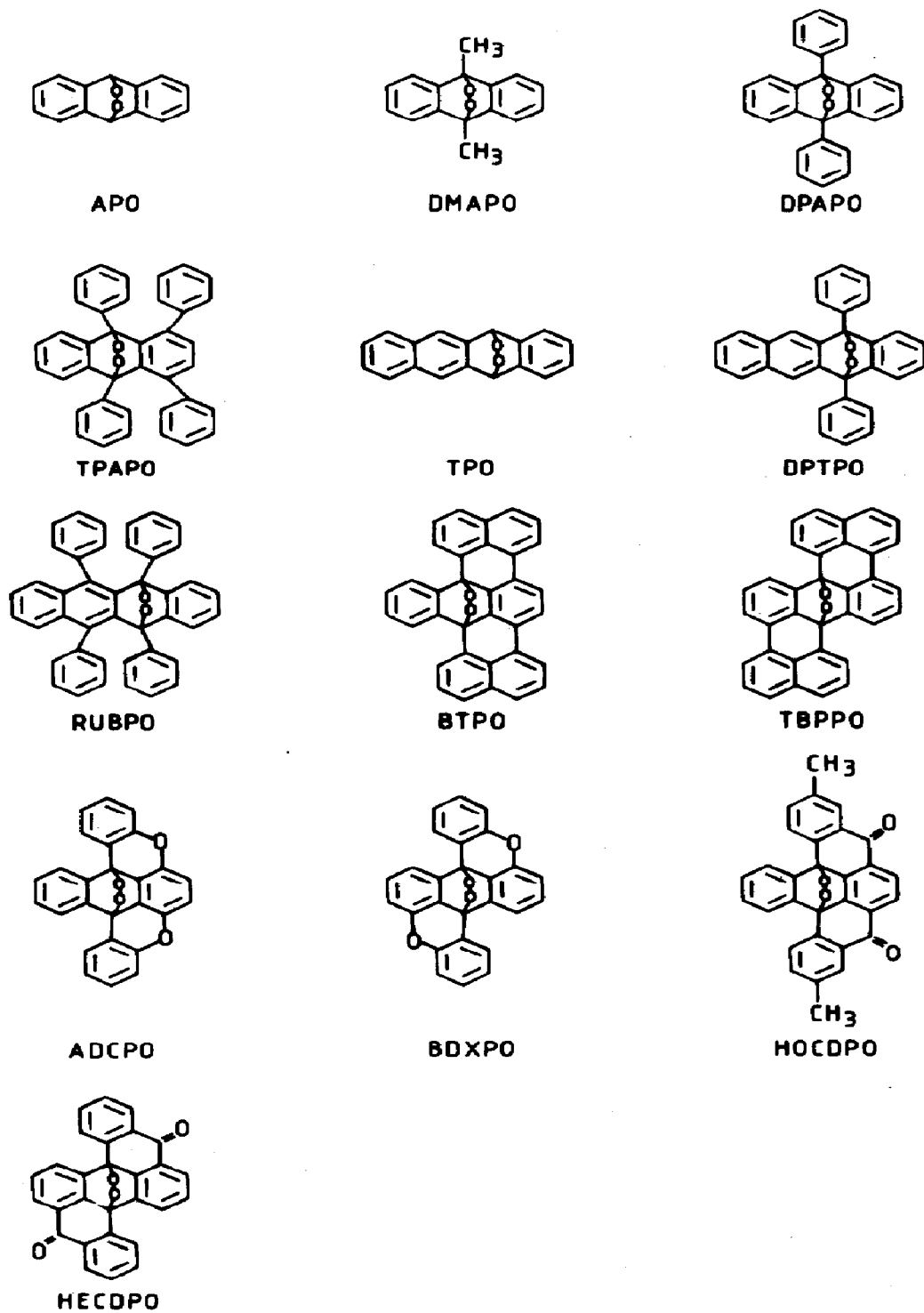
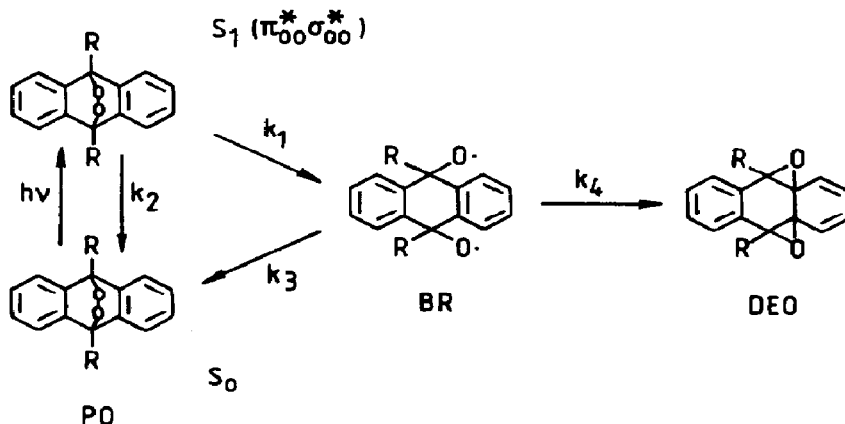


Fig. 1. Structures of the endoperoxides investigated in this study.

phenyl. A further strong reduction is observed if the phenyl substituents are connected rigidly to the anthracene frame as is the case for the lowest six endoperoxides of Table 1.

A realistic explanation of this effect is that the increase in space for the substituents and the stabilization of the molecular frame by the additional connecting groups prevents or at least minimizes the formation of the strongly stressed ring system of the primary rearrangement product diepoxide [12]. However, a strong substituent effect on the O—O bond cleavage appears to be highly improbable.

For a quantitative interpretation, the possibility of re-formation of ground state endoperoxide by back reaction of the biradical has to be included into the kinetic scheme, since only in case of competition between forward and back reaction will the substituent effect operate on  $Q_{dec}(S_1)$ . The following kinetic scheme, which differs from Rigaudy's ideas only by the inclusion of the possible additional back reaction of the biradical, satisfactorily interprets the photochemical rearrangement.



(PO is the endoperoxide, BR is the biradical and DEO is the diepoxide.)

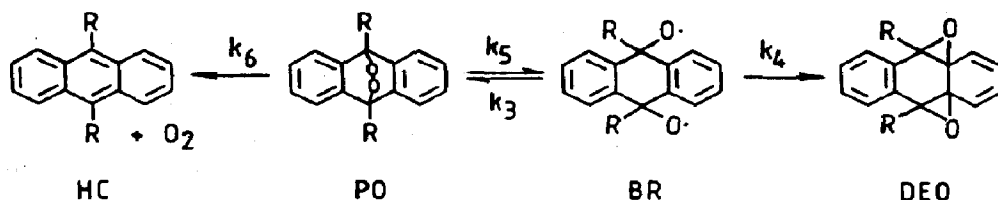
Upon excitation of the peroxide chromophore, O—O bond cleavage occurs either directly from  $S_1(\pi_{00}^* \sigma_{00}^*)$  or indirectly from the corresponding triplet state with a rate constant  $k_1$ .  $k_2$ ,  $k_3$  and  $k_4$  are the rate constants of  $S_1 \rightarrow S_0$  IC of the endoperoxide, of back reaction of the biradical to the endoperoxide and of forward reaction of the biradical intermediate to the diepoxide. Thus

$$Q_{dec}(S_1) = \frac{k_1}{k_1 + k_2} \frac{k_4}{k_3 + k_4} = qe \quad (7)$$

where  $q$  is the primary quantum yield of biradical formation and  $e$  is the efficiency of rearrangement of the biradical.

A very similar kinetic scheme is proposed to explain the thermal rearrangement. In contrast to Rigaudy's conception, which again assumes only a forward reaction of the biradical, our scheme includes a chemical

equilibrium between the endoperoxide and the biradical, which of course is completely shifted to the endoperoxide.



(HC is the parent aromatic hydrocarbon.)

$k_3$  and  $k_4$  are already known from the photochemistry scheme.  $k_5$  and  $k_6$  are the rate constants of thermal O—O bond cleavage and of cycloreversion respectively.

The thermal yield  $A_c$  of cycloreversion is defined as the ratio of the concentration  $[\text{HC}]_{\text{max}}$  of aromatic hydrocarbon formed during complete endoperoxide thermolysis and the initial endoperoxide concentration  $[\text{PO}]_0$ . Equation (8) can be derived from our kinetic scheme for  $A_c$ :

$$A_c = \frac{[\text{HC}]_{\text{max}}}{[\text{PO}]_0} = \frac{k_6}{k_5 e + k_6} \quad (8)$$

Thus eqn. (9) results for the thermal yield of rearranged products:

$$A_{\text{dec}} = \frac{k_5 e}{k_6 + k_5 e} \quad (9)$$

#### 4.2. Photochemical rearrangement

As can be seen in Fig. 2, a rather good linear correlation exists between  $Q_{\text{dec}}(S_1)$  and  $A_{\text{dec}}$ , which extends over two orders of magnitude, although the common rearrangement precursor biradical is produced in two completely different ways: photochemically or thermally. This indicates that the substituent effect at least predominantly operates on the thermal reactions of the biradical and thus on  $e$ , and not on the primary reaction.

This conclusion, however, has important consequences for the primary quantum yield  $q$  of biradical formation. If the graduations in  $Q_{\text{dec}}(S_1)$  are only caused by different  $e$  values, it follows that  $q$  has to be constant for all endoperoxides, according to eqn. (7). Since  $Q_{\text{dec}}(S_1)$  reaches maximum values of unity for APO and TPO, this means that  $q = 1$  for all endoperoxides for which the photochemical rearrangement is described correctly by the kinetic scheme given above. This conclusion excludes radiative deactivation and postulates a pure chemical deactivation of the  $S_1(\pi^*_{00}\sigma^*_{00})$  state even for endoperoxides with low  $Q_{\text{dec}}(S_1)$ .

Actually, for HECDDPO, which has the lowest value of  $Q_{\text{dec}}(S_1)$  of all endoperoxides investigated so far, neither fluorescence nor phosphorescence could be observed upon  $S_1$  excitation even in an oxygen-free matrix at 77 K. The other five lowest endoperoxides of Table 1 have also been investigated with respect to fluorescence in DCM at room temperature. In each case, no



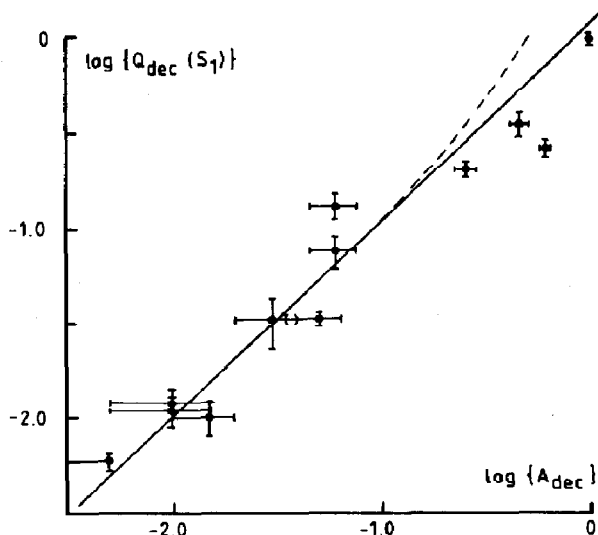


Fig. 2. Plot of  $\log \{Q_{\text{dec}}(S_1)\}$  against  $\log A_{\text{dec}}$  for 13 endoperoxides ( $\times$ , experimental value with error bars; the data points of TPO and APO coincide). The straight line results from a linear least-squares fit (slope, 1.03; coefficient of determination, 0.96). The broken line was calculated according to eqn. (10) with  $k_5 = k_6$ .

emission could be detected. These results confirm impressively our conclusions derived above.

Since for the photochromic endoperoxides radiative deactivation of  $S_1$  does not occur and IC to  $S_0$  is highly improbable because of the large energy gap of about  $23\,000\text{ cm}^{-1}$ , chemical deactivation by O—O bond breakage and subsequent O—O bond formation must take place, originating either directly from  $S_1(\pi^*_{00}\sigma^*_{00})$  or indirectly after intersystem crossing from  $T_1(\pi^*_{00}\sigma^*_{00})$ .

It was demonstrated by means of triplet-triplet energy transfer experiments as a function of temperature [23], triplet-sensitizer energy [23, 24] and triplet-acceptor energy [24] that the  $T_1(\pi^*_{00}\sigma^*_{00})$  state of peroxides is actually of purely repulsive nature, leading to O—O bond breakage. These results are in accordance with complete neglect of differential overlap calculations for hydrogen peroxide, which indicate that three excited singlet states and four triplet states exhibit no minima with changes in the O—O distance and correlate with the ground state of two hydroxyl radicals [25].

The conclusions of the theoretical investigation also support a chemical deactivation mechanism for the  $S_1$  state of endoperoxides, occurring directly on the repulsive  $S_1(\pi^*_{00}\sigma^*_{00})$  energy surface, although our results may also be explained by an indirect chemical deactivation on the repulsive triplet energy surface.

Thus, to the best of our knowledge, endoperoxides appear to be the first class of compounds for which deactivation in the condensed phase of the  $S_1$  state to  $S_0$  occurs exclusively chemically and not physically.

### 4.3. Thermal rearrangement

The efficiency  $e$  of rearrangement of the biradical may be approximated by  $Q_{\text{dec}}(S_1)$  since  $q = 1$  holds for the primary quantum yield of splitting of the endoperoxide. Substituting  $e = Q_{\text{dec}}(S_1)$  into eqn. (9) leads to

$$Q_{\text{dec}}(S_1) = \frac{k_6 A_{\text{dec}}}{k_5(1 - A_{\text{dec}})} \quad (10)$$

Equation (10) gives a relation between the photochemical yield and the thermal yield of rearrangement for each endoperoxide. However, it must be kept in mind that the  $Q_{\text{dec}}(S_1)$  (at about 20 °C) and the  $A_{\text{dec}}$  (at 139 °C) were determined at different temperatures. Therefore eqn. (10) is only correct if the ratio  $e = k_4/(k_3 + k_4)$  is temperature independent.

The double logarithmic plot in Fig. 2 demonstrates the rather good linear correlation found experimentally between the  $Q_{\text{dec}}(S_1)$  and the  $A_{\text{dec}}$ . Linear least-squares fitting results in the straight line plotted in Fig. 2 having a slope  $m = 1.03$ .

Equation (10) predicts a linear correlation only for low  $A_{\text{dec}}$  ( $A_{\text{dec}} < 0.1$ ) and a constant ratio  $k_6/k_5$ . With  $k_5 = k_6$ , for low  $A_{\text{dec}}$ , eqn. 10 results in a straight line for the plot of  $\log\{Q_{\text{dec}}(S_1)\}$  against  $\log A_{\text{dec}}$  with slope  $m = 1$ , which almost coincides with the fitted straight line of Fig. 2. For high  $A_{\text{dec}}$ , however, eqn. (10) leads to a deviation to larger  $Q_{\text{dec}}(S_1)$ , which is shown as the broken curve in Fig. 2.

Since our data are described rather well by eqn. (10), it seems that at least for low  $A_{\text{dec}}$  either both assumptions of temperature independent  $e$  values and of  $k_5 = k_6$  hold true or that deviations from these assumptions cancel each other out. The first alternative appears to us to be the more probable. But even if this is not the case, it is found that thermal O—O bond cleavage also occurs for endoperoxides with low  $A_{\text{dec}}$ , with rate constants  $k_5$  which are of the same order of magnitude as the corresponding rate constants  $k_6$  of thermal cycloreversion. The only reason for the preferential formation of the hydrocarbon and O<sub>2</sub> cycloreversion products lies in the reduction in the rate constant  $k_4$  of the reaction leading to the diepoxide because of steric hindrance due to bulky substituents in the 9,10-position, whereas the rapid back reaction ( $k_3$ ) to the endoperoxide remains unaffected.

### 4.4. Competition between cycloreversion and rearrangement

Our present knowledge of the photochemical and thermal reactions of endoperoxides of aromatic hydrocarbons is summarized in Fig. 3. The ordinate gives a linear energy scale. On the abscissa the O—O distance is plotted on a non-linear scale increasing from the left to the right. Consequently the lowest electronic states of the hydrocarbon—O<sub>2</sub> contact pair are drawn on the left-hand side, whereas in the middle the energy level scheme of the endoperoxide is depicted, from which the rearrangement pathways lead to the right. DPAPPO was taken as being a typical endoperoxide of the anthracene series and was used as the example. The energy barriers

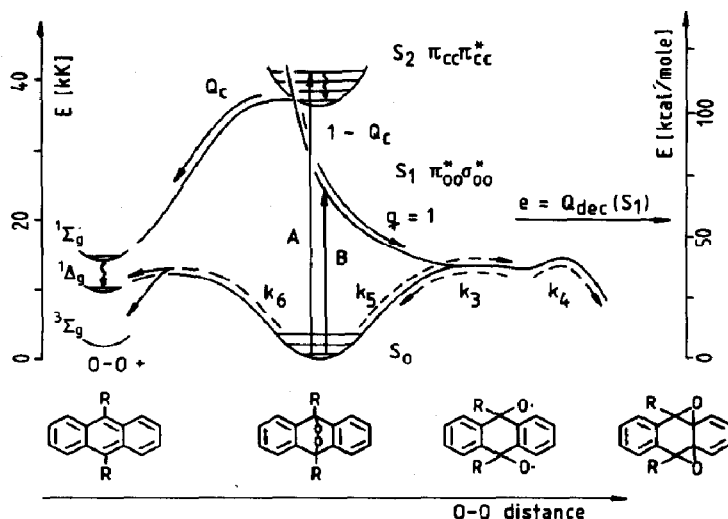


Fig. 3. Potential energy curves for the photochemical and thermal reactions of endoperoxides of aromatic hydrocarbons, demonstrated for DPAPO as the example; for a description see the text.

surrounding the ground state of DPAPO in both directions are chosen to fit the activation enthalpy of cycloreversion ( $\Delta H^\ddagger = 33 \text{ kcal mol}^{-1}$  [5]) and to be slightly larger than the O—O bond dissociation enthalpy ( $\Delta H = 36 \text{ kcal mol}^{-1}$  [23]). The ground state enthalpy differences of the contact pair and of the biradical compared with that of the endoperoxide were adjusted to  $5 \text{ kcal mol}^{-1}$  [5] and to  $36 \text{ kcal mol}^{-1}$ . The small barriers surrounding the biradical minimum were chosen arbitrarily.

Upon excitation of the  $\pi_{cc}\pi_{cc}^*$  states of DPAPO (A in Fig. 3), cycloreversion occurs with  $Q_c$  from the thermalized  $S_2(\pi_{cc}\pi_{cc}^*)$  state yielding the parent hydrocarbon and  $^1\text{O}_2$ . The competing IC leads to  $S_1$  with the quantum yield  $1 - Q_c$ . The purely repulsive  $S_1(\pi_{oo}^*\sigma_{oo}^*)$  state, however, may also be selectively excited by irradiation (B in Fig. 3). Because there is no minimum on the potential energy surface the  $S_1$  state of PO is dissociative, and the biradical is formed with the primary quantum yield  $q = 1$ , before physical deactivation to  $S_0$  can take place.

Two competing thermal reactions are possible for the biradical, leading either to the diepoxide or back to the endoperoxide in its ground state. Therefore the deactivation of the electronically excited endoperoxide via the repulsive energy surface of  $S_1$  by O—O bond breakage and subsequent O—O bond formation is a chemical process.

$e = Q_{dec}(S_1)$  is obtained for the efficiency  $e$  of rearrangement of the intermediate biradical to give the diepoxide. If the substituents R are connected rigidly to the anthracene frame,  $e$  decreases because of an increase in steric hindrance reducing the rate constant  $k_4$  for the reaction from the biradical to the diepoxide.

The thermal rearrangement of the endoperoxide also proceeds through the biradical intermediate; however, it is produced in a different way. A

chemical equilibrium exists between the endoperoxide and the biradical, which is completely shifted to the endoperoxide. Thermal rearrangement is not selective, since cycloreversion competes and hydrocarbon and O<sub>2</sub> are formed, the latter partially in an excited singlet state. The yields of cycloreversion and rearrangement depend on the ratio  $k_6/k_5$  and on  $e$ . Even for photochromic endoperoxides ( $A_e \approx 1$ ;  $e \approx 0$ ) homolytic splitting of the O—O bond occurs since  $k_6$  and  $k_5$  are of the same order of magnitude. Only for endoperoxides with a large tendency to rearrange ( $A_{dec} \approx 1$ ) must  $k_6$  be significantly smaller than  $k_5$ .

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