

THE PHOTOOXIDATION OF 1,4-DIMETHOXY-9,10-DIPHENYL-ANTHRACENE AND THE CHEMILUMINESCENT DECOMPOSITION OF ITS ENDOPEROXIDE

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Summary

The kinetics of the thermal decomposition of the 1,4-endoperoxide of 1,4-dimethoxy-9,10-diphenylanthracene (DMDPA) were studied in several solvents. It was found that the photooxidation-decomposition cycle was free of side reactions in benzene, ethyl acetate and dimethylformamide. The chemiluminescence which accompanies the decomposition of the peroxide is due to the fluorescence of the regenerated DMDPA. The photochemical decomposition of the peroxide excited at 330 nm as well as the photooxidation of DMDPA at the same wavelength led to the same equilibrium mixture of the two components.

1. Introduction

Among the several aromatic hydrocarbons which can be photooxidized in solution to give endoperoxides, 1,4-dimethoxy-9,10-diphenylanthracene (DMDPA) has received particular attention in the past, partly because the thermal decomposition of its peroxide can be readily achieved at moderate temperatures. This reaction regenerates the parent hydrocarbon but side reactions have been observed during both photooxidation and decomposition [1 - 5]. It seems to be well established that the endoperoxide formed is the one linking the carbon atoms 1 and 4 [4, 5] (Fig. 1). It has also been reported that the thermal decomposition is accompanied by chemiluminescence [2 - 5] but the species responsible for this emission was not identified. Some data on the thermal decomposition of I have been published but only in a fragmentary form [6, 7].

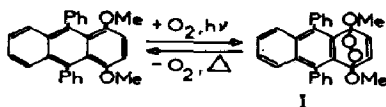


Fig. 1. Formation of the endoperoxide.

Since no detailed kinetic study of the decomposition reaction in solution has been published, nor an assessment of the degree of reversibility of the oxidation-decomposition cycle in various media, we decided to examine the details of these processes. The present study aims therefore at completing the understanding of this system and at establishing the best experimental conditions for the achievement of a clean reversible cycle.

2. Experimental

The synthesis of DMDPA was carried out using the route described by Dufraisse and Velluz [3] with minor modifications (m.p. 201 °C, literature value [3] 203 °C). The solvents used were purified and dried by standard techniques.

Experiments were started by preparing solutions of DMDPA (about 1×10^{-4} mol dm⁻³) and taking their electronic spectra in the region 280 - 470 nm (Beckman Acta M VI). The 1 cm quartz cells containing these solutions were then irradiated at 0 °C for 20 min with a 60 W tungsten lamp held a few centimetres from the cells. A new spectrum was taken to establish the extent of photooxidation and thereafter the cells were left in the spectrophotometer compartment and the regeneration of DMDPA was followed at constant temperature (± 0.5 °C) by monitoring the increase in optical density at 377 and 406 nm as a function of time. Full spectra were also frequently taken during the reactions. In order to study the reversibility of the cycle in each solvent, some reaction mixtures were left until a constant spectral intensity was reached during the thermal decomposition; then a second photooxidation was carried out, followed by a new complete study of the decomposition etc. for several cycles. Luminescence spectra were taken with a FOCI Mark I spectrofluorimeter provided with a thermostated cell compartment. Higher concentrations of DMDPA were used for these experiments.

3. Results

Typically, the irradiation of DMDPA solutions produced conversions to the endoperoxide of 80 - 90%. The reactions did not need any oxygen other than that present in air-saturated solvents. The thermal decomposition always proceeded smoothly giving first order plots linear up to about 90% recovery of the starting material in the solvents in which reversibility was good. The reaction was studied in ethyl acetate, benzene, dimethylformamide (DMF) and butanone.

Full reversibility of the photooxidation-decomposition cycle was observed with the first three solvents, while in butanone only about 80% of the initial DMDPA was recovered after each cycle. Chlorinated alkanes were also tried but with these solvents the rapid disappearance of DMDPA was not accompanied by the corresponding formation of the endoperoxide I.

The absorption spectrum of DMDPA was the same in the four solvents used for kinetic measurements, except for small variation of the extinction coefficients. A typical spectrum of the starting compound is shown in Fig. 2, curve 2, with its two characteristic maxima at 377 and 406 nm. The extinction coefficients ($\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) for the peak at 377 nm were 7800 in ethyl acetate, 8050 in benzene and butanone and 7200 in DMF. The absorption spectrum of the endoperoxide I is shown in Fig. 2 curve 3 and amplified in Fig. 2 curve b. The weak transition centred at 330 nm had an extinction coefficient of about $1100 \text{ mol}^{-1} \text{dm}^3 \text{cm}^{-1}$.

The course of a typical decomposition reaction is also shown in Fig. 2. The progressive reappearance of the DMDPA spectrum and the corresponding disappearance of the peroxide band are uniquely interconnected, as indicated by the occurrence of four isosbestic points at 332, 328, 299 and 294 nm (see curves b and c).

A detailed kinetic study of this process was carried out. Values of the first order rate constant in different media and at different temperatures are given in Table 1 together with the Arrhenius parameters for ethyl acetate and DMF. The Arrhenius plot for the experiments in ethyl acetate is shown in Fig. 3. Reactions in benzene and butanone gave the same rates as in ethyl acetate, within experimental errors. The effect of residual moisture in the reaction medium was also investigated in view of the possibility of hydrolysis of the endoperoxide raised by Dufraisse *et al.* [4]. We found that in ethyl acetate the rate of thermal decomposition was unaffected either by thorough drying of the solvent or by addition of up to 2% water.

Since it has been reported that the thermal decomposition of endoperoxide I is accompanied by luminescence [2 - 5], it was decided to identify the origin of this emission. In both benzene and ethyl acetate a measurable luminescence was obtained at 60°C from endoperoxide solutions of concentration about $10^{-2} \text{ mol dm}^{-3}$, the signal being more intense in benzene. The spectra obtained from these experiments were the same as those resulting from emission of DMDPA solutions excited in the region 350 - 430 nm. A typical spectrum is shown in Fig. 4.

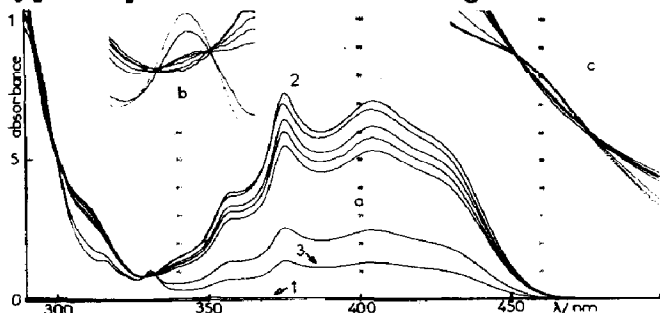


Fig. 2. Curve 1, baseline; curve 2, spectrum of DMDPA before photooxidation and at the end of thermal decomposition; curve 3, spectrum of the endoperoxide (about 80%) with some residual DMDPA (about 20%) after photooxidation. The spectra between curves 3 and 2 were scanned while the thermal decomposition of the endoperoxide was progressing. Curve b, amplification of endoperoxide absorption region. Curve c, amplification of region between 290 and 300 nm. Solvent, ethyl acetate.

TABLE 1

Kinetics of the thermal decomposition of endoperoxide I

Solvent ethyl acetate		Solvent dimethylformamide	
T ($^{\circ}\text{C}$)	k (s^{-1})	T ($^{\circ}\text{C}$)	k (s^{-1})
20	3.9×10^{-6}	50	4.2×10^{-4}
30	1.4×10^{-5}	60	1.6×10^{-3}
40	6.5×10^{-5}	70	3.0×10^{-3}
50	2.1×10^{-4}		
60	9.0×10^{-4}		

$E = 113 \text{ kJ mol}^{-1}$	$E = 89 \text{ kJ mol}^{-1}$
$A = 10^{14.7} \text{ s}^{-1}$	$A \approx 10^{11} \text{ s}^{-1}$

k is the first order rate constant obtained from spectroscopic measurements of DMDPA regeneration. The results in benzene and butanone were the same as in ethyl acetate.

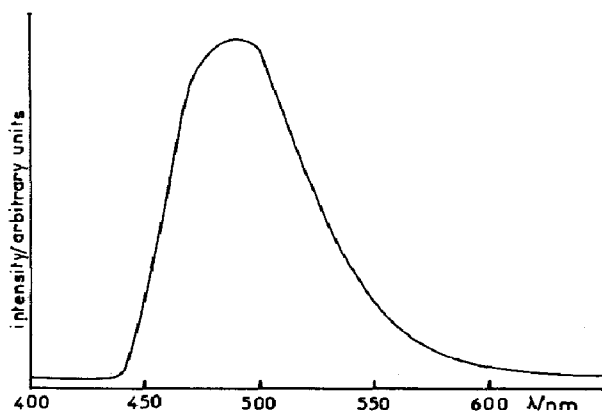
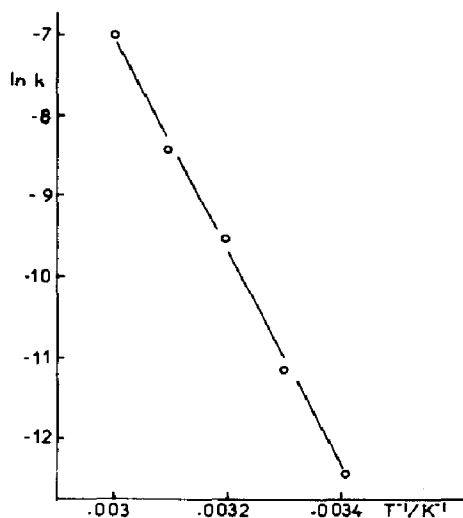


Fig. 3. Arrhenius plot for the thermal decomposition of the endoperoxide in ethyl acetate.

Fig. 4. The emission spectrum of DMDPA excited between 350 and 430 nm in benzene and the luminescence spectrum of an endoperoxide solution being decomposed at 60 $^{\circ}\text{C}$ in benzene.

The photochemical decomposition of endoperoxide I was also studied by irradiating its solutions at 330 nm. It was found that DMDPA was formed in these processes and that its reappearance was accompanied by both its typical emission spectrum (Fig. 4) and additional weaker emission bands between 380 and 395 nm. These reactions reached an equilibrium, *i.e.* a constant ratio of peroxide to DMDPA. Irradiation of DMDPA solutions at 330 nm slowly gave the endoperoxide I, the same equilibrium being reached.

Finally, photooxidation-decomposition experiments were carried out in ethyl acetate with 10^{-4} mol dm $^{-3}$ of DMDPA and 10^{-1} mol dm $^{-3}$ of 2,2,4-trimethylpentene-2. At 60 °C both reactions proceeded at the same rate as in the absence of olefin and no difference in the spectra was noticed.

4. Discussion

Contrary to previous conclusions [1 - 5], it appears that we can effectively prepare the endoperoxide I by photochemical oxidation of DMDPA at 0 °C without the interference of side reactions, provided appropriate solvents are chosen. Chlorinated hydrocarbons cannot be used in this context because they react with the excited DMDPA probably through chlorine atom abstraction to give radical chain reactions which destroy the substrate. These interactions predominate over photooxidation given the overwhelming concentration effect in favour of the solvents.

The thermal decomposition of endoperoxide I can also be made to proceed smoothly and completely in appropriate solvents. Thus, in ethyl acetate, benzene and DMF we can repeat the oxidation-decomposition cycle several times without appreciable loss of DMDPA in side reactions. The Arrhenius parameter obtained for the thermal decomposition of I are quite typical for reactions of this type [8]. The lower activation energy obtained with DMF must be related to a better solvation of the transition state by this highly polar solvent. The occurrence of isobestic points in reactions involving these three solvents confirms the negligible (if any) role of side reactions.

In contrast, the partial irreversibility of the cycle in butanone shows that either this solvent can interact mildly with excited DMDPA or its peroxide, or some residual impurity acted as quencher in one of the reactions of the cycle. At present we have no evidence in favour of either possibility.

The chemiluminescence which accompanies the thermal decomposition of I is obviously due to fluorescence from the excited DMDPA singlet state, given the identity of the chemiluminescence spectrum and the fluorescence spectrum obtained by direct irradiation of DMDPA. Thus, the thermal decomposition of I generates excited singlet DMDPA.

The observation that the endoperoxide I can also be effectively decomposed by photochemical activation had been forecast by Rigaudy [5] and is not surprising, given the energy involved in the absorption of a 330 nm photon. The attainment of an equilibrium in this reaction and in the corresponding photooxidation of DMDPA excited at 330 nm simply shows that, since the latter absorbs weakly at that wavelength, both reactions are effectively activated by illuminating a mixture of DMDPA and I under these conditions and standard concentrations of both species are reached at a given temperature upon attainment of chemical equilibrium. The emission at 380 - 395 nm is probably due to an excited state of I.

The experiment in the presence of an excess of olefin shows that singlet oxygen is not involved in the photooxidation reaction but does not give any

indication of its possible formation in the thermal decomposition of I. A search for hydroperoxides arising from the reaction of the olefin with such an intermediate was not carried out because of the low concentration of DMDPA used. However, Wasserman and Scheffer [9] have reported that the endoperoxide of 9,10-diphenylanthracene decomposes generating singlet oxygen.

Further studies related to the possible applications of this convenient oxygen-fixing/oxygen-releasing system will be the subject of future work.

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