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REACTIONS ORIGINATING FROM DIFFERENT UPPER EXCITED SINGLET STATES: THE PHOTOCYCLOREVERSION OF THE ENDOPEROXIDES OF 1,4-DIMETHYL-9,10-DIPHENYLANTHRACENE

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Summary

The photocycloreversion of the two isomeric endoperoxides of 1,4-dimethyl-9,10-diphenylanthracene (DMDPA), PO1 with the peroxide bridge in the 9,10-position and PO2 with the peroxide bridge in the 1,4-position, was investigated as a function of irradiation wavelength. The cycloreversion quantum yield Q_c was found to be almost constant over the range of the $S_2(\pi\pi^*)$ absorption band for PO1 with a maximum value $Q_c = 0.26$ at 290 nm, indicating that cycloreversion occurs from the thermalized S_2 state. For PO2 a stepwise increase in Q_c with photon energy was observed with a maximum value $Q_c = 0.57$ at 250 nm. The approximately wavelength-independent values of Q_c correlate energetically with different $\pi\pi^*$ absorption bands, revealing that cycloreversion of PO2 originates from mainly thermalized S_2, S_3 and S_4 states.

The direct formation of S_1-excited DMDPA in the photocycloreversion of PO2 was investigated using steady state techniques. A quantitative evaluation of our experimental data for 290 and 266 nm led to the finding that no S_1-excited DMDPA is formed, in contrast to the results of previously published time-resolved studies on the photolysis of PO2.

1. Introduction

The photochemical cycloreversion of endoperoxides (POs) of aromatic compounds resulting in the re-formation of the parent hydrocarbon (HC) and oxygen is distinguished from common solution phase photochemistry by two conspicuous features: the reaction originates from upper excited singlet states S_n ($n \geqslant 2$) and in addition takes place adiabatically since ground state HC and singlet oxygen ($^1O_2$) are produced in equal amounts.

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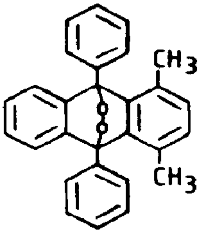
We have established these exceptional features of PO photochemistry in a series of investigations on POs of different structure [1 - 4].

POs can be classified into two groups from the pattern of the wavelength variation of the cycloreversion quantum yields Q_c, which depends on the excited states from which the cycloreversion reaction originates.

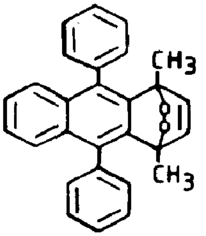
For POs of anthracene derivatives, which possess a symmetrical π electronic structure with respect to the O—O bond axis, cycloreversion starts only from the lowest $\pi\pi^*$ state, this being the S_2 state [2, 5, 6].

In contrast, for some asymmetric POs having different π electronic chromophores adjacent to both sides of the peroxide bridge, cycloreversion obviously originates from several upper excited singlet states S_n $(n \geqslant 2)$ which may be vibrationally hot or thermally equilibrated [4, 6, 7].

The correlation found between the number of electronic states leading to cycloreversion and the symmetry of the π electronic structure is based on investigations of the POs corresponding to different HCs. In order to eliminate substituent effects it is of great interest to compare the photochemistry of POs of symmetrical and asymmetrical π electronic structure which are derived from the same HC. We have studied the two isomeric POs of 1,4-dimethyl-9,10-diphenylanthracene (DMDPA); PO1 possesses an approximately symmetrical π electronic structure with respect to the peroxide bridge, whereas PO2 is asymmetrical.



PO1



PO2

Recently Eisenthal's group published the first time-resolved study of the photolysis of a PO [8]. They reported that photocycloreversion of PO2 yields adiabatically S_1-excited DMDPA in less than 5 ps.

The upper time limit set by this study lies well within the expected time range for reactions occurring from upper excited electronic states. However, it was very surprising to us that DMDPA should be produced directly in the S_1 state. Indeed, we found cycloreversion of POs to be an adiabatic photoreaction only with respect to the $^1O_2$ formed. For none of the POs investigated did we observe immediate fluorescence of the corresponding HC at the beginning of photolysis, which would be expected if S_1 HC were formed directly by cycloreversion [1, 4, 9].

Of course, it may be that among POs PO2 is an exception in this respect. If this is so, steady state measurements should complement and confirm the dynamic results. However, if production of S_1-excited DMDPA is not observed in steady state experiments, the upper time limit of 5 ps given for photocycloreversion will be invalidated.

Both objectives, the consideration of the correlation between the number of reactive electronic states and the symmetry of the π electronic structure of a PO as well as the complementation of the time-dependent measurements on the photocycloreversion of PO2 by steady state measurements, seemed to us to be worth pursuing so we have investigated the photolysis of PO1 and PO2.

2. Experimental details

DMDPA, PO1 and PO2 were prepared following literature procedures [10, 11]. CH_2Cl_2 (Merck, spectroscopic grade) was used as the solvent in all the experiments.

Preliminary experiments showed that the presence of O_2 did not have any effect on the quantum yield of cycloreversion. Therefore all irradiations were carried out at 22 ± 3 °C in air-saturated solutions. Photochemical quantum yields were determined using the instrument described in ref. 12. For the irradiation wavelengths 260, 270 and 323 nm, however, the set-up was modified by using an irradiation source consisting of an XBO 150 xenon lamp and a 1 m double grating monochromator (RSV) instead of an HBO 100 mercury lamp and the Schoeffel 0.25 m grating monochromator. The determination of the monochromatic quantum fluxes was performed by applying a calibrated photodiode and a recently developed UV actinometer [13] (Actinochrome R (248/334) from PTI, Tornesch). During the quantum yield experiments, the formation of DMDPA was followed using a Perkin–Elmer 555 spectrophotometer. Conversions of DMDPA usually amounted to 0.4% but never exceeded 2% PO1 and 1% PO2. If necessary, corrections were made for internal filter effects resulting from DMDPA formation. Fluorescence measurements were performed using a computer-controlled Perkin–Elmer 650-40 fluorescence spectrophotometer.

3. Results and discussion

3.1. Excited electronic states leading to cycloreversion

In Figs. 1 and 2 the electronic spectra and the wavelength dependences of the quantum yields Q_c of cycloreversion are shown for PO1 and PO2; the behaviour differs markedly in both cases, as a result of their different π electronic structures.

3.1.1. Spectra

POs of aromatic HCs are bichromophoric or multichromophoric compounds. The electronic and spatial separation of the different chromophores is accomplished by the two carbon atoms next to the peroxide bridge.

Generally, the PO transition lowest in energy is the $\pi^*\sigma^*$ transition occurring in the peroxide chromophore. The corresponding $S_0 \rightarrow S_1$ absorp-

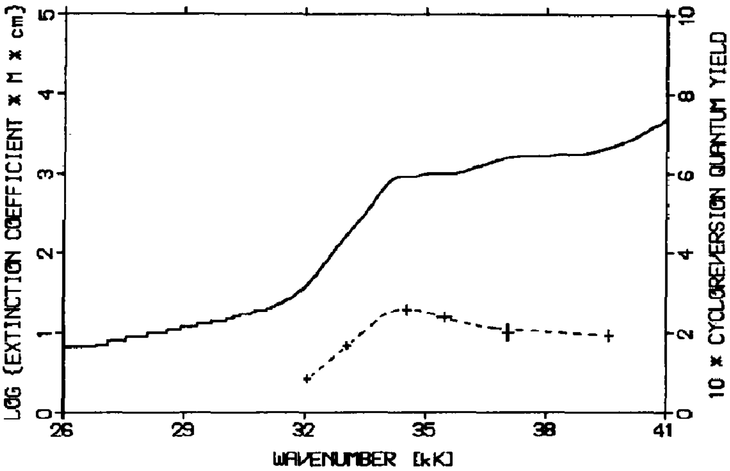


Fig. 1. Electronic spectrum of PO1 (solvent, CH_2Cl_2). Photon energy dependence of Q_c: +, experimental value with error bars.

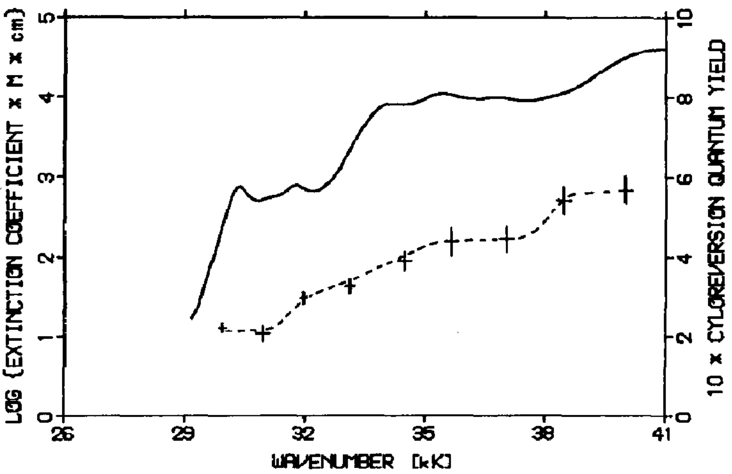


Fig. 2. Electronic spectrum of PO2 (solvent, CH_2Cl_2). Photon energy dependence of Q_c: +, experimental value with error bars.

tion band extends with very low extinction coefficients $\epsilon \leqslant 10\ M^{-1}\ cm^{-1}$ down to about 23 000 cm^{-1} [5, 14]. Only for POs containing aromatic chromophores with an excitation energy of at least 33 000 cm^{-1} can this absorption band be detected definitely (see Fig. 1).

The substantial differences in the electronic structures of PO1 and PO2 result from the different π electronic systems of the chromophores remaining from the anthracene system.

For PO1 there are four chromophores with benzene-like π electronic systems. Although the aromatic rings are surrounded by a different number of substituents, only small effects on the $\pi\pi^*$ excitation energies will result since the substituents are sp^3-bound carbon atoms. Actually the electronic spectrum of PO1 is very similar to the spectra of anthracene endoperoxide '(APO), 9,10-dimethylanthracene endoperoxide (DMAPO) and 9,10-diphenylanthracene endoperoxide (DPAPO) [5, 6]. Therefore, for PO1 to a good approximation the energy levels of the aromatic chromophores are degenerate, and this compound may be classified as a PO of symmetrical π electronic structure with respect to the peroxide bond axis.

Because of the symmetry and of the small number of UV-excitable transitions of benzene-like chromophores, PO1 has a rather simple energy level scheme. The 0–0 $\pi\pi^*$ singlet transitions can be localized at the low energy onsets of the corresponding absorption bands: $S_0 \rightarrow S_2$ at about 34 000 cm^{-1} and $S_0 \rightarrow S_3$ at about 40 000 cm^{-1}.

Although the weak absorption of the peroxide chromophore is almost hidden by the stronger $\pi\pi^*$ bands in the spectrum of PO2, the $\pi^*\sigma^*$ transition at about 23 000 cm^{-1} is still the $S_0 \rightarrow S_1$ excitation. In contrast to PO1, two $\pi\pi^*$ chromophores of very different excitation energy result for PO2, these being the 1,4-diphenylnaphthalene and the ethylene chromophores. The ethylene chromophore does not absorb UV radiation below 42 000 cm^{-1}. Therefore only the substituted naphthalene chromophore determines the absorption. Since the spectrum of PO2 resembles much more the spectrum of naphthalene than that of 1,4-diphenylnaphthalene, it seems that both methyl substituents of PO2 effect a 90° twist of the phenyl substituents with respect to the naphthalene plane, decoupling the π electronic systems.

Consequently, 0–0 $\pi\pi^*$ singlet transitions occur at about 30 000 cm^{-1} ($S_0 \rightarrow S_2$), 33 000 cm^{-1} ($S_0 \rightarrow S_3$) and about 39 000 cm^{-1} ($S_0 \rightarrow S_4$) and are localized on the naphthalene chromophore.

3.1.2. *Quantum yields of cycloreversion*

In analogy to the electronic spectra, the wavelength dependences of the Q_c of the two POs are markedly different. This result is in accordance with investigations on the photolysis of PO1 and PO2, which were carried out independent of us and at the same time by Eisenthal's group [15].

For PO1, in the region of overlap of the absorptions of the peroxide and the aromatic chromophores, Q_c increases significantly with photon energy and reaches a maximum value $Q_c^M = 0.258 \pm 0.013$ at 34 500 cm^{-1}. On the high energy side Q_c decreases slightly to a value $Q_c = 0.194 \pm 0.015$ at 39 600 cm^{-1}.

Very similar photon energy dependences of Q_c and Q_c^M have already been determined in CH_2Cl_2 for APO ($Q_c^M = 0.22$), DMAPO ($Q_c^M = 0.35$) and DPAPO ($Q_c^M = 0.22$) and the same interpretation can now be applied to PO1 [5, 6]. Cycloreversion originates only from the thermalized lowest excited $\pi\pi^*$ singlet state (S_2) and has to compete with the interchromophoric internal conversion (IC) to S_1 ($\pi^*\sigma^*$), which is not reactive towards cycloreversion. From vibrationally hot S_2 states, additional deactivation processes occur that are probably chemical in nature, leading to a reduction in Q_c.

A much more structured energy dependence of Q_c is obtained for PO2. At least three different almost wavelength-independent plateaux can be detected ranging from 30 000 to 31 000 cm^{-1} with $Q_c \approx 0.21$, from 34 500 to 37 000 cm^{-1} with $Q_c \approx 0.42$ and from 38 500 to 40 000 cm^{-1} with $Q_c \approx 0.55$.

Only very few examples of stepwise wavelength dependences of quantum yields have been reported up to now [4, 6, 16, 17]. Among these are the photocycloreversion reactions of the asymmetrical POs of 1,4,9,10-tetraphenylanthracene (TPAPO) and of 1,4-dimethoxy-9,10-diphenylanthracene (DDAPO) [4, 6]. For the asymmetrical POs of the tetracene series Q_c values continually increasing with photon energy have been reported [7].

These strange patterns of wavelength dependence indicate that there must exist several upper electronically and perhaps vibrationally excited states from which cycloreversion occurs. Actually these compounds are distinguished by high densities of $\pi\pi^*$ singlet states in the investigated irradiation range.

With the exceptions of DDAPO and of PO2 this results from the fact that different aromatic chromophores are combined in one PO. The excitation of each of the two chromophores connected in the β position to the oxygen atoms of the peroxide bridge can lead to cycloreversion. The competing IC from the lowest excited singlet state of each aromatic chromophore to a lower singlet state of a different chromophore is an interchromophoric process which, owing to insufficient orbital overlap, can be slow enough for cycloreversion to take place from the upper excited singlet state.

However, cycloreversion must be a very rapid process which even competes efficiently with intrachromophoric IC. This is demonstrated convincingly by the example of PO2. The only $\pi\pi^*$ chromophore of PO2 bound in the β position to both oxygen atoms, which can be excited with energies below 40 000 cm^{-1}, is the naphthalene chromophore. If only excitation of the lowest $\pi\pi^*$ singlet state should lead to cycloreversion one would expect a photon energy dependence of Q_c similar to that of PO1, *i.e.* approximate wavelength independence above $S_2(\pi\pi^*)$. As can be seen in Fig. 2, this is not the case. Q_c increases in at least three steps. Each plateau can be correlated with a different electronic transition: the first plateau with $S_0 \rightarrow S_2$, the second with $S_0 \rightarrow S_3$ and the third with $S_0 \rightarrow S_4$, which are the ^1L_b, ^1L_a and ^1B_b transitions in the naphthalene chromophore. From the observation that each plateau with only weak wavelength dependence of Q_c begins at the low energy onset of the corresponding absorption bands and that the intermediate areas with strong wavelength dependence of Q_c are in the overlapping regions of the consecutive bands, one can conclude that cycloreversion actually occurs from mainly thermalized upper excited states.

The contribution of each of the different excited states to cycloreversion can be estimated roughly from the Q_c plateau values using the method of evaluation given in ref. 6. From S_2, cycloreversion occurs with an efficiency of about 0.21, which is approximately the same as the value for PO1. However, from S_3 and from S_4, cycloreversion, which is assumed to compete only with IC to the next lower singlet state, also takes place with the surprisingly high efficiencies of 0.27 and 0.22 respectively. Because intrachromophoric IC $S_4 \rightarrow S_3$ and $S_3 \rightarrow S_2$ may be expected to be faster than interchromophoric IC, we suppose cycloreversion to proceed with a rate higher from S_4 and S_3 than from S_2.

Since cycloreversion of POs can therefore originate even from the upper excited electronic states of each aromatic chromophore, the correlation between the number of reactive electronic states and the symmetry of the π electronic structure appears to be very simple. For POs of the anthracene series, which possess a symmetrical π electronic structure with respect to the O—O bond axis, such as PO1, there is only one $\pi\pi^*$ singlet state in the photon energy range investigated. The next higher $\pi\pi^*$ singlet state lies at about 40 000 cm^{-1} or higher. In contrast, for asymmetrical POs the $\pi\pi^*$ singlet state density is much higher below 40 000 cm^{-1}. However, cycloreversion can only (but must not) originate effectively from the upper excited singlet states of aromatic chromophores, as can be seen in the photochemistry of photochromic endoperoxides [18].

3.2. *Formation of S_1-excited DMDPA in the photocycloreversion of PO2*

In principle the quantitative determination of S_1-excited HC during photocycloreversion is a simple experiment in steady state photochemistry. One only has to compare the emission spectra of a pure PO and of a pure HC solution under identical experimental conditions. If the emission spectrum of the PO matches the fluorescence spectrum of the HC and if the absorbances of both solutions at the chosen excitation wavelength are the same, then the fraction f of S_1-excited HC with respect to the total amount of HC generated is given by

$$f = \frac{I_c^{PO}(0)}{Q_c I_F^{HC}} \qquad (I)$$

where $I_c^{PO}(0)$ is the emission intensity of the pure PO solution at the beginning of irradiation and I_F^{HC} is the fluorescence intensity of the HC solution, each measured at the maximum of the HC fluorescence.

The experiment becomes more complicated if solutions of thermally labile POs are contaminated by small amounts of thermally produced HC. In addition one even has to expect a build-up in HC contamination because of the actinic effect of the exciting radiation.

Therefore we determined the concentration [HC] of HC contamination before and after exposing the PO2 solution to actinic UV radiation, by fluorescence spectrophotometry under conditions in which photocycloreversion of PO2 does not take place ($\lambda_{exc} = 385$ nm; $\lambda_{em} = 450$ nm). Emission experiments were performed at the excitation wavelengths 290 nm and 266 nm. The solutions were stirred continuously during irradiation to prevent inhomogeneity effects.

290 nm was selected because at this wavelength the extinction coefficient of PO2 is larger than that of DMDPA ($\epsilon_{PO2}/\epsilon_{DMDPA}(290) = 1.4$) and the cycloreversion quantum yield was determined ($Q_c(290) = 0.39$). 266 nm

TABLE 1

Evaluation of the fraction f of S_1-excited DMDPA with respect to the total DMDPA formed in the photocycloreversion of PO2

	λ_{exc} = *290 nm*	λ_{exc} = *266 nm*
$[PO2]_0$ (M)	3.16×10^{-5}	3.16×10^{-5}
$[HC]_0{}^{a}$ (M)	$(1.30 \pm 0.07) \times 10^{-7}$	$(1.20 \pm 0.06) \times 10^{-7}$
$I_E{}^{PO}(0)^{b}$	0.070 ± 0.005	0.34 ± 0.01
$[PO2]_\infty$ (M)	3.13×10^{-5}	3.15×10^{-5}
$[HC]_\infty{}^{a}$ (M)	$(4.4 \pm 0.2) \times 10^{-7}$	$(2.4 \pm 0.1) \times 10^{-7}$
$I_E{}^{PO}(\infty)^{b}$	0.214 ± 0.005	0.70 ± 0.01
$\Delta[HC]$ (M)	$(3.1 \pm 0.2) \times 10^{-7}$	$(1.2 \pm 0.1) \times 10^{-7}$
$\Delta I_E{}^{PO} = \Delta I_F{}^{HC\ b}$	0.144 ± 0.007	$0.36 \pm 0.01_4$
$\Delta I_F{}^{HC}/\Delta[HC]$ (M^{-1})	$(4.65 \pm 0.6) \times 10^5$	$(3.0 \pm 0.4) \times 10^6$
$I_F{}^{HC}(0)^{b,c}$	0.06 ± 0.008	0.36 ± 0.05
$I_c{}^{PO}(0)^{b,d}$	0.01 ± 0.01	-0.02 ± 0.05
$I_F{}^{HC\ e}$	20.9	11.4
f	0.0012 ± 0.0012	$-0.003_5 \pm 0.009$

The indices 0 and ∞ indicate values at the beginning and at the end of irradiation respectively. For further details see the text.

[a] Determined via HC fluorescence at 450 nm (λ_{exc} = 385 nm).

[b] Emission from PO2 solution at 450 nm (λ_{exc} = 290 nm or λ_{exc} = 266 nm).

[c] Calculated from $\Delta I_F{}^{HC}/\Delta[HC]$ and $[HC]_0$.

[d] $I_c{}^{PO}(0) = I_E{}^{PO} - I_F{}^{HC}(0)$.

[e] Fluorescence of DMDPA at 450 nm (λ_{exc} = 290 nm or λ_{exc} = 266 nm).

was chosen since Eisenthal's experiments had been performed at this wavelength. However, at 266 nm the extinction coefficient ratio is much worse ($\epsilon_{PO2}/\epsilon_{DMDPA}(266) = 0.14$) and Q_c has to be interpolated from the respective values at 260 nm and 270 nm ($Q_c(266) = 0.5$).

Table 1 lists the results of our investigations. The contamination of PO2 by DMDPA at the beginning of irradiation amounted to $[HC]_0 = 1.2 \times 10^{-7}$ M. During irradiation, HC contaminations increased in each experiment owing to photocycloreversion. However, the conversions $\Delta[HC]$ were so small that the PO2 concentrations [PO2] and the absorbances at the respective excitation wavelengths remained almost constant. Therefore the emission intensities $I_c{}^{PO}$ resulting from S_1-excited DMDPA produced directly by cycloreversion of PO2 should also be constant. Since the observed emission intensities $I_E{}^{PO}$ of the PO2 solutions became larger with irradiation time, the increases $\Delta I_E{}^{PO}$ originate from the fluorescence of the DMDPA formed during the experiment, $\Delta[HC]$.

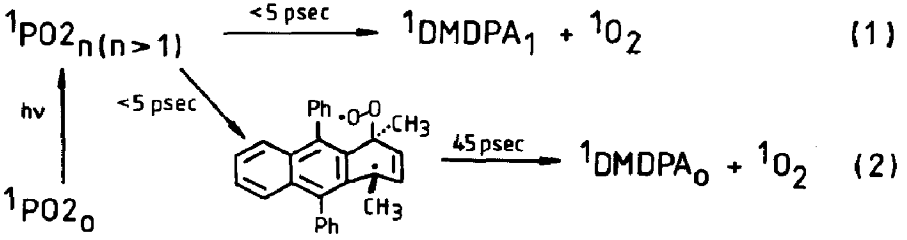
Consequently $\Delta I_E{}^{PO} = \Delta I_E{}^{HC}$. This was additionally checked by recording the fluorescence excitation spectra. From the ratios $\Delta I_F{}^{HC}/\Delta[HC]$ and the initial contaminations $[HC]_0$ the contributions of contamination fluorescences $I_F{}^{HC}(0)$ to the total emission intensities $I_E{}^{PO}(0)$ at the beginning of the irradiations can be calculated. $I_F{}^{HC}(0)$ has to be subtracted from $I_E{}^{PO}(0)$ to get $I_c{}^{PO}(0)$, the emission intensity resulting from S_1-excited DMDPA produced by photocycloreversion. From the $I_c^{PO}(0)$ values and the fluorescence intensities I_F^{HC} of pure DMDPA solutions having the same absorbances at λ_{exc} as the PO2 solutions, and from the Q_c values, the fractions f were determined by using eqn. (I).

Independent of the excitation wavelength, we obtain $f = 0$ within the limits of error. In other words, *no* S_1-excited DMDPA is produced directly by cycloreversion of PO2. From a measurement with smaller error limits a maximum limit of about 0.2% can be derived for the fraction f of S_1-excited DMDPA with respect to the total DMDPA formed.

This result agrees with earlier investigations on different POs [1, 4, 9]. Indeed, with respect to the $^1O_2$ formed, photocycloreversion of POs is an adiabatic reaction. Although energetically possible, no S_1-excited HC is actually produced. Following spin conservation rules one has to presume that in this adiabatic photoreaction only ground state HC develops.

Our result disagrees completely with the previous paper on the photolysis of PO2 by Einsenthal's group, in which only the prompt (in less than 5 ps) production of S_1-excited DMDPA was reported [8].

In a later article on the same subject, which was brought to our attention by the referee of this paper, Eisenthal's group extended their photocycloreversion reaction scheme by including the path leading to the formation of ground state DMDPA [19]. They observed that S_0 DMDPA is produced by 266 nm pulse photolysis with a much slower rise time of 45 ± 15 ps. Competition between the fast adiabatic production of S_1 DMDPA (reaction (1)) and the slow formation of S_0 DMDPA (reaction (2)) was proposed (see Scheme 1), the first reaction being less important than the second by roughly a factor of 10. In order to explain the low efficiency of the fast reaction (1) an even faster C—O bond cleavage leading to a biradical intermediate was proposed for reaction (2). In the subsequent reaction this biradical precursor should then give S_0 DMDPA and $^1O_2$, with a decay time of 45 ps.



Scheme 1.

Our results, however, disagree with this paper too; that roughly 10% of the DMDPA formed should be produced adiabatically in its S_1 state contrasts sharply with the maximum limit of 0.2% determined by us. This discrepancy of a factor of 50 lies far beyond the limits of error of our experiment.

We believe that the only reasonable explanation for the prompt (in less than 5 ps) DMDPA fluorescence observed by Eisenthal's group during the

266 nm pulse photolysis of PO2 is the excitation of DMDPA present from the beginning as a contaminant of the PO2. These researchers have been aware of this possible artifact and tried to rule it out by looking for DMDPA fluorescence following 355 nm pulse excitation [8]. They actually found the DMDPA impurity fluorescence; however, it was regarded as negligible. But the experimenters did not take into account that the extinction coefficient of DMDPA at 266 nm is larger than that at 355 nm by a factor of 15; therefore the contamination fluorescence at the wavelength of investigation is of course also larger by a factor of 15 and this probably cannot be neglected.

From our experiments, in which inner filter effects due to DMDPA contamination and DMDPA build-up have been considered carefully, it is found that at most only 0.2% of the DMDPA formed is produced directly in the S_1 state. If one still accepts the photocycloreversion reaction scheme proposed by Eisenthal's group [19], the rupture of the first C—O bond (reaction (2)) has to occur about 500 times faster than the adiabatic splitting into S_1 DMDPA and $^1O_2$, which is claimed to last less than 5 ps (reaction (1), in order to explain consistently the large differences in the efficiencies of formation of S_1 DMDPA (0.2% or below) and S_0 DMDPA (about 100%). Therefore the biradical has to be formed in less than 10 fs (10^{-14} s). Since the overall quantum yield of DMDPA production amounts only to about 50% at 266 nm it follows that radiationless deactivation (probably IC from S_n) should occur with a similar rate.

However, IC from S_n ($n \geqslant 2$) to S_1 is usually expected to proceed slower in organic molecules in solution (10^{-13} s or longer). On the basis of this expectation the probability of competition between direct S_1 DMDPA production and biradical formation in the photolysis of PO2 appears to be low.

The conventional paradigm of very rapid deactivation of upper excited electronic states by IC (in 10^{-13} s or less, depending on the energy gap) is based on estimates and theoretical considerations rather than on experiments [20]. However, owing to the recent advances in the field of picosecond laser techniques, the experimental investigation of radiationless deactivation processes of large organic molecules in the condensed phase has become promising.

Surprisingly, the first results seem to indicate that even if IC is an intrachromophoric process it is much slower than expected. For example, Rulliere *et al.* observed decay times for IC fom S_3 and S_4 to S_1 of perylene of the order of 50 - 60 ps [21]. No significant solvent effects on IC could be detected on changing the polarity and the viscosity of the solvent. Drexhage and Sens investigated the dependence of the radiationless decay $S_1 \rightarrow S_0$ for a large number of Rhodamine, pyranine, oxacine, carbacine and cyanine dyestuffs on their respective energy gaps (7000 - 18 000 cm^{-1}) [22]. They found an excellent linear correlation between the logarithm of the IC rate and the energy gap. Decay times of IC ranging from about 10 ps to about 100 ns have been evaluated. In view of these recent unexpected results it becomes necessary to revise our customary ideas concerning the rate of IC.

A comparison of the order of magnitude of the experimentally determined IC decay times with the value estimated for the competitive biradical mechanism (10 fs) shows that this mechanism leads to unrealistic results in PO2 photocycloreversion.

In contrast, a simple competitive mechanism, which we established in a series of detailed studies by means of photostationary experiments [1 - 7, 18] leads to a consistent picture of product quantum yield, product rise time and the recent experimentally determined IC decay times. This mechanism only assumes competition between cycloreversion and IC from the reactive singlet states S_n ($n \geqslant 2$) to the S_{n-1} states and finally to S_1.

With an overall cycloreversion quantum yield $Q_c = 0.5$ at 266 nm, the formation of S_0 DMDPA and the competing IC from S_3 to S_1 is expected to proceed with a similar rate. Actually, the rise time of 45 ps observed by Eisenthal and coworkers fits very well into the time range now expected for the interchromophoric IC transition $S_3(\pi\pi^*) \rightarrow\rightarrow S_1(\pi^*\sigma^*)$, which should be rather slow because of only poor orbital overlap.

Acknowledgments

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