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Journal of Photochemistry and Photobiology A: Chemistry 193 (2008) 25–32
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Self-sensitized photo-oxidation of *para*-indenylidene–dihydropyridine derivatives

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Received 21 February 2007; received in revised form 12 May 2007; accepted 1 June 2007
Available online 7 June 2007

Abstract

The photo-oxidation of 1-butyl-4-(1H-inden-1-ylidene)-1,4-dihydropyridine (BIDP) and its 2-methyl derivative (BIMDP) by molecular oxygen is reported. The quantum yields are small, ranging from 10^{-3} to 10^{-5}, depending on solvent and irradiation wavelength. Oxidation is assigned to the reaction of the ground state molecules with singlet oxygen ($O_2(^1\Delta_g)$) labeled hereafter as $^1O_2$ which is produced in turn by energy transfer from the indenylidene–dihydropyridine derivatives triplet state. In the absence of competing processes, the chemical yield of the oxidation can be very high for elongated irradiation. The reaction quantum yield depends on solvent polarity, being significantly larger in polar solvents than in non-polar ones. Photo-sensitization experiments using benzophenone to produce $^1O_2$ show that the rate constant for singlet oxygen reaction with BIDP is also solvent dependent, increasing with polarity. A tentative mechanism accounting for the small quantum yield of the photo-oxidation is proposed. The major deactivation process of the initially excited singlet after optical excitation is internal conversion, whose rate constant is several orders of magnitude larger than the rate constants of intersystem crossing and of fluorescence. The larger oxidation yield in polar solvents compared to non-polar ones is mainly due, according to the proposed mechanism, to the more efficient oxidation of the substrates by $^1O_2$ in polar solvents.

Keywords: Photo-oxidation; Singlet oxygen; Intersystem crossing; Internal conversion; Quantum yield; Sensitization; Solvent polarity effect

1. Introduction

BIDP and BIMDP belong to a family of molecules that may be considered as nitrogen analogs of sesquifulvalenes. They are characterized by very intense absorption band in the visible range, and upon irradiation at this band neither fluorescence nor photochemical activity were reported. The photochemical stability and negligible fluorescence intensity indicate very rapid and efficient internal conversion (IC) to the ground state. We became interested in these compounds as a conical intersection is predicted to mediate this fast process. A simple model calculation on CPHDP, which may be considered as the parent compound of BIDP and BIMDP (see Fig. 1), indicates that the curve crossing responsible for the conical intersection may be removed in a polar environment [1,2]. We therefore initiated an experimental study of the photochemistry of these compounds. Preliminary experiments indicated that although the molecules are photo-stable in an inert atmosphere, in air-equilibrated solutions irradiation at the visible absorption band leads to de-coloration of the solution. The rate and yield of this bleaching, tentatively assigned to photo-oxidation, were found to depend on the solvent and also on the irradiation wavelength. In this paper we report our mechanistic studies of this photo-reaction and propose a model that accounts for the solvent effect.

The indenylidene–dihydropyridines are molecules in which a dihydropyridine moiety is linked to an indene group via a formal double bond (Fig. 1). The molecules have a relatively high dipole moment in the ground state, rationalized by a large contribution of a polar VB structure shown in Fig. 1b. These strongly colored molecules were first synthesized and characterized over 40 years ago [3,4].

Solutions of both BIDP and BIMDP in organic solvents are indefinitely stable in an oxygen atmosphere in the dark, and also photo-stable when irradiated in the absence of O_2; in contrast, it was found early on that although the quantum yield of the reaction is quite small, complete oxidation can be induced

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doi:10.1016/j.jphotochem.2007.06.003

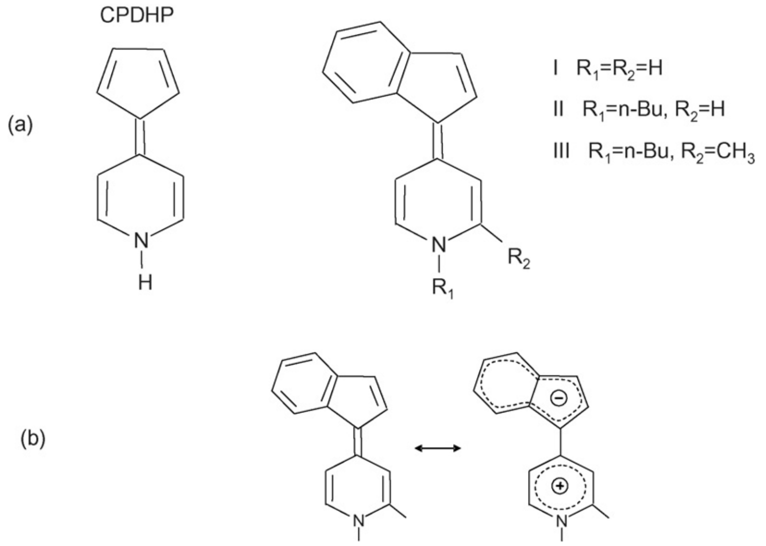

Fig. 1. (a) The molecular structure of CPDHP (left) and the title compounds (right); II is BIDP and III is BIMDP; (b) the covalent and zwitterion VB structures of I that contribute to the electronic wave-function of the compound.

by extended irradiation. The oxidation process which is thus due to a minor deactivation channel of the initially excited singlet state, might serve as a probe for the main deactivation process—internal conversion which is mediated by a conical intersection [1].

As in all ethylene derivatives, photo-excitation is likely to be followed by *E*–*Z* isomerization. BIMPD was chosen for this study as it has an asymmetric structure, allowing in principle separating the *E* and *Z* isomers from each other. It was hoped that electronic excitation might lead to two spectroscopic distinguishable isomers allowing the study of the photo-isomerization dynamics. However it turned out that the two isomers have very similar absorption spectra making it impractical to track the reaction using the visible absorption spectrum. In addition, the two isomers have similar enthalpies of formation and a rather low barrier along of the thermal reaction exchanging them (from the NMR data of Ref. [4], a barrier for interconversion of the two isomers can be estimated to be about 25 kcal/mol). In this paper we therefore assume that the two isomers are in rapid thermal equilibrium at room temperature, existing as a 1:1 mixture.

2. Experimental details

The molecules were prepared and purified following literature procedures [3]. They were characterized by their visible, IR and NMR spectra as well as by elemental analysis. Irradiation was performed either by a cw 450 W xenon high pressure lamp (Oriel Model 6261, whose irradiance between 350 and 500 nm is almost constant) or by the third harmonic (355 nm) of a pulsed Nd:YAG laser (10 ns, up to 30 mJ/pulse). In the lamp experiments, light was passed through a water cell (acting as a heat shield) and then through an appropriate colored filter, irradiation time was typically 30–60 min. The transmission spectra of the filter combinations used are shown in Fig. 2 along with the absorption spectrum of BIPD. Actinometry was done using a ferric(III) oxalate actinometer [5]. Since broadband filters were used, the variation of the filter transmittance and the absorbance of the solution were corrected for. The reaction progress was followed by monitoring the visible absorption band of the reactant; attempts to isolate and characterize the oxidation products by means of chromatography (HPLC, TLC, GC–MS) failed. Unless otherwise stated, all photochemical runs were made using air-saturated solutions. The solvents used were hexanes, cyclohexane (CH), methylcyclohexane (MCH, Sigma–Aldrich, spectroscopic grade), 2-methyl-pentane (2 MP, Fluka AG, purum), methyl-cyclopentane (MCP, Fluka AG, purum) ethylacetate (EA, Sigma–Aldrich, spectroscopic grade), acetonitrile (MeCN, J.T. Baker, HPLC grade).

In the photo-sensitization experiments, singlet oxygen was generated using benzophenone as a sensitizer and the third harmonic of the Nd:YAG laser for excitation; $^1O_2$ was monitored by the emission of the forbidden $^1\Delta_g - {}^3\Sigma_g{}^-$ transition using a germanium photo-diode (New Focus Model 2033, 30 μs time constant). A narrowband interference filter centered on 1270 nm was used to reduce scattered light.

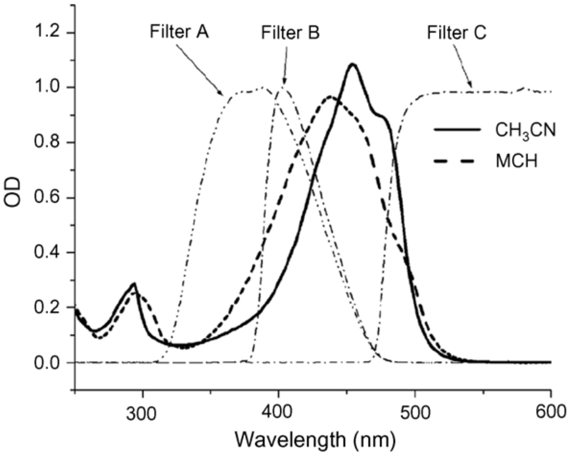

Fig. 2. The spectrum of BIDP in MeCN and in MCH and the transmission spectra of Filter combinations A, B and C used in the experiments.

Table 1
Photo-oxidation quantum yields of BIDP (4×10^{-5} M)[a]

Solvent	Φ(OX) (Filter A)	Φ(OX) (Filter B)
MCH	1.8×10^{-5}	2.1×10^{-5}
THF	7.1×10^{-5}	3.8×10^{-5}
EA	2.7×10^{-4}	7.3×10^{-5}
MeCN	3.9×10^{-4}	8.7×10^{-5}

[a] Estimated error 15%.

Table 2
Photo-oxidation quantum yields of BIMDP (4×10^{-5} M)[a]

Solvent	Φ(OX) (Filter A)	Φ(OX) (Filter C)
2MP	9.0×10^{-5}	7.1×10^{-5}
MCP	7.0×10^{-5}	7.0×10^{-5}
MCH	1.1×10^{-4}	6.5×10^{-5}
THF	2.2×10^{-4}	1.1×10^{-4}
EA	3.8×10^{-4}	1.8×10^{-4}
MeCN	8.6×10^{-4}	2.0×10^{-4}

[a] Estimated error 15%.

3. Experimental results

3.1. Direct photo-oxidation

The UV–vis spectra of BIDP and BIMDP are almost indistinguishable, that of BIDP was shown in Fig. 2. Irradiation by a filtered xenon lamp (Filter A) of the compound in the presence of oxygen (air-saturated solution) leads to gradual discoloration in polar solvents; in non-polar solvents the bleaching is much slower. As seen from Tables 1 and 2, the quantum yields for photo-oxidation, Φ(OX), are higher in the more polar solvents, especially when irradiating in the high frequency part of the absorption spectrum. The absolute values of the quantum yields are rather small (all $< 10^{-3}$) indicating competition with a much more efficient deactivation process.

Attempts (using the nanosecond laser) to observe a transient absorption, which might be due to a triplet state, were unsuccessful in all solvents.

3.2. Quenching experiments

In an attempt to elucidate the mechanism of the oxidation reaction, several possible quenchers were used. Piperylene (PP), aliphatic amines (TEA, TMA) and sodium azide (NaN_3) are well known quenchers of triplet states [6] and of $^1O_2$ [7]. The data were analyzed using the Stern–Volmer equation (Eq. (1)) that yielded a straight line when the photochemical yield was plotted against the concentration of the quencher:

$$\frac{\phi(0)}{\phi(Q)} = 1 + K_{SV}[Q] \qquad (1)$$

Here K_{SV} is the Stern–Volmer constant given by

$$K_{SV} = k_Q \tau_0 \qquad (2)$$

with k_Q being the bimolecular quenching rate constant and τ_0 is the lifetime of the excited state involved in the reaction in the absence of the quencher.

The results of the quenching experiments are reported in Table 3; the data refer to the change in overall reaction yield as measured from the decrease in the absorbance of the substrate. The fifth column reports values of k_Q assuming that the quenched species is $^1O_2$ using literature data for its decay time in different solvents. The sixth column lists calculated τ_0's assuming diffusion controlled quenching rate constants.

3.3. Sensitized oxidation

In order to estimate the potency of singlet oxygen as an oxidizer of BIDP and BIMDP, benzophenone (BP) was used as a sensitizer. The reaction rate constant for the BIDP oxidation by singlet oxygen in MeCN was determined by measuring the decay times of the singlet oxygen emission signal at 1270 nm in solutions containing different BIDP concentrations. In typical experiment the air-saturated solutions of BP (10^{-3} M) and BIDP ($0–2 \times 10^{-5}$ M) were irradiated by a pulsed Nd–YAG laser at 355 nm in a quartz flow cell and the averaged (10^4 shots) singlet oxygen emission signals were detected by the IR detector and recorded by an oscilloscope (Fig. 3). The solutions were flown at a rate ensuring minimal reaction so that the BIDP concentration was constant during the experiment. The singlet oxygen emission decay time becomes shorter at larger BIDP concentrations. The analysis of the results was accomplished using Stern–Volmer equation (2) where the quenching constant k_Q is assumed to be identified with the rate constant of BIDP oxidation by singlet oxygen, and τ_0 is the singlet oxygen lifetime at the absence of BIDP.

Substitution of the literature value for the singlet oxygen lifetime in MeCN (80 μs[8]) and the Stern–Volmer constant from our experiments $(88 \pm 5) \times 10^3$ in Eq. (2) yields the rate constant

Table 3
Product quenching results

Molecule	Quencher	Solvent	K_{SV} (M^{-1})[a]	k_Q(M^{-1} s^{-1})[b]	τ_0 (s)[c]
BIDP	NaN_3	MeCN	2.7×10^4	3.4×10^8	1.4×10^{-6}
BIDP	NMe_3	MeCN	1.3×10^5	1.6×10^9	6.8×10^{-6}
BIMDP	NaN_3	MeCN	1.8×10^4	2.3×10^8	1.0×10^{-6}
BIMDP	PP	EA	1.7	3.8×10^4	1.1×10^{-10}
BIMDP	PP	*n*-Hexane	0.5	1.6×10^4	2.4×10^{-11}

[a] Estimated error 20%.

[b] Assuming that the quenched species is $^1O_2$ and the following lifetimes: 80 μs in MeCN [8], 45 in EA [9], 31 μs in hexane [10], 23 μs in cyclohexane [11].

[c] Assuming diffusion controlled quenching rate constants.

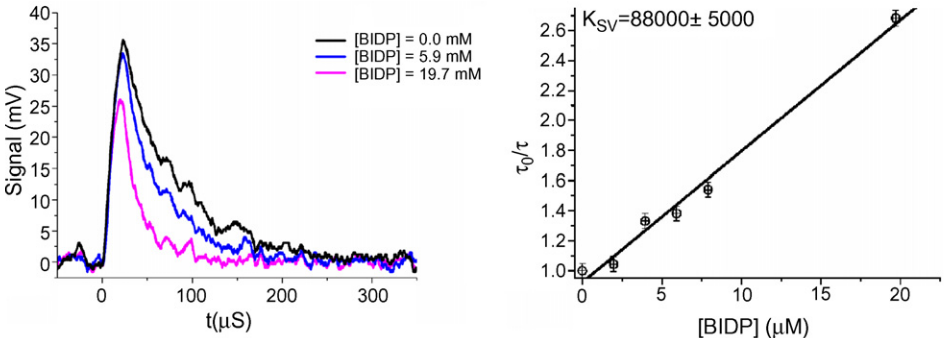

Fig. 3. Quenching singlet oxygen with BIDP in air-saturated MeCN. Left panel: singlet oxygen emission signals at different BIDP concentrations. Right panel: a Stern–Volmer plot of the data.

for BIDP oxidation by singlet oxygen in MeCN ($k_{\mathrm{OX}}^{\mathrm{CN}}$) to be $(1.10 \pm 0.06) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Unfortunately the slow response of the detector and the shorter lifetime the singlet oxygen in hexane solution (~31 μs[10]) did not allow the direct evaluation of the reaction constant in hexanes. In order to estimate the rate constant in hexane, comparative steady state photo-oxidation experiments were carried out in which benzophenone (10^{-3} M) was added to 4×10^{-5} M BIDP O_2-saturated solutions in MeCN and in hexane. The solutions were irradiated at 355 nm and the bleaching rate of the BIDP visible band was followed as a function of time. The results of these experiments are presented in Fig. 4. From the slopes of the initial absorption change it was

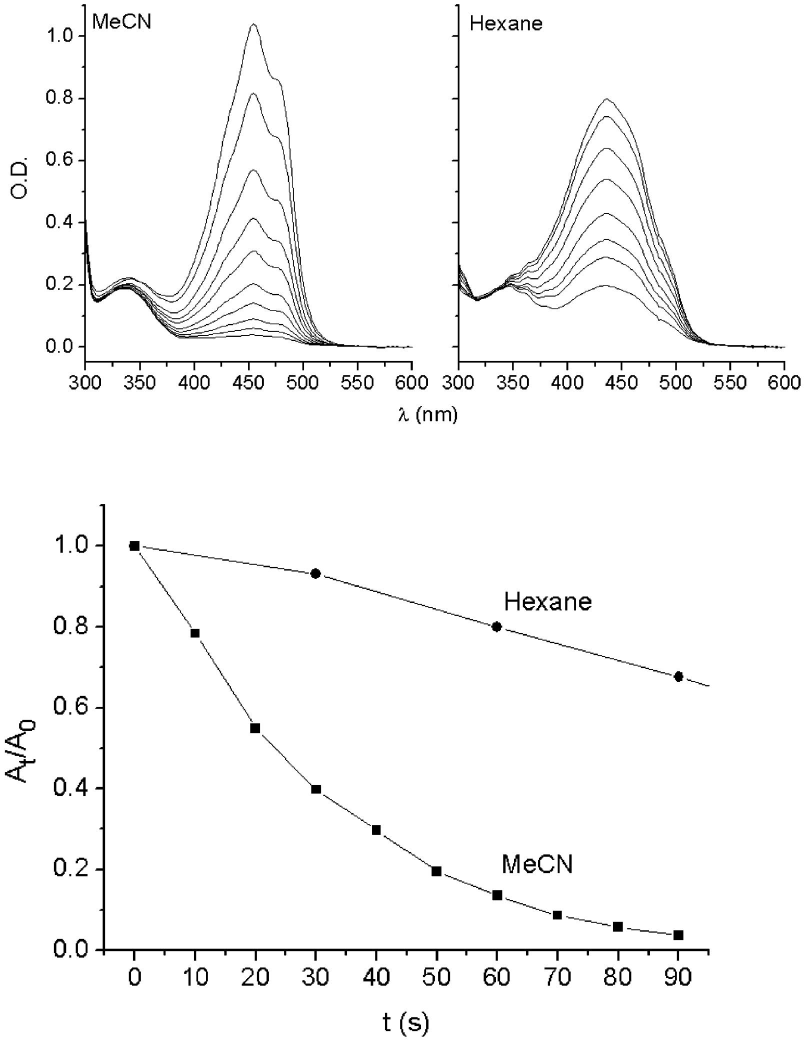

Fig. 4. Steady state sensitized photo-oxidation of BIDP in MeCN and hexane O_2-saturated solutions. Upper left panel: Sensitized photo-bleach of the BIDP in MeCN solution (spectra recorded at 10 s intervals); Upper right panel: Sensitized photo-bleach of the BIDP in hexane solution (spectra recorded at 30 s intervals); Bottom panel: The BIDP photochemical conversion vs. time in MeCN ($A_0 = 1.04$) and hexane ($A_0 = 0.79$). A_t is the optical density after irradiation for t (s).

found that the quantum yield in MeCN was 12.5 times larger than in hexane.

In control experiments, the same solutions were irradiated in the absence of molecular oxygen using nitrogen-saturated solutions. Some bleaching was observed in hexane and none in MeCN; the rate of bleaching in hexane was much smaller than in the presence of molecular oxygen. In other control experiments the solutions were irradiated at 355 nm in the absence of benzophenone. In these cases the bleaching rate was also negligible compared to the rate in the presence of benzophenone.

The above results can be interpreted on the base of the following kinetic scheme for the sensitized BIDP photo-oxidation:

$$BP(S_0) + h\nu \rightarrow BP(S^*) \tag{3}$$

$$BP(S^*) \rightarrow BP(T_1) \quad \left(k^{S}_{ISC,S}\right) \tag{4}$$

$$BP(T_1) \rightarrow BP(S_0) \quad \left(k^{S}_{ISC,S} + k_P\right) \tag{5}$$

$$BP(T_1) + {}^3O_2 \rightarrow BP(S_0) + {}^1O_2 \quad (k_{ET}) \tag{6}$$

$${}^1O_2 \rightarrow {}^3O_2 \quad (k_D) \tag{7}$$

$$P + {}^1O_2 \rightarrow \text{oxidation products} \quad (k_{OX}) \tag{8}$$

The quantum yield of the singlet oxygen sensitization by BP (Eqs. (3)–(6)) is equal to 0.3 independent of the solvent [12]. Eq. (7) describes the uni-molecular and solvent-induced deactivation processes (k_D) and Eq. (8) BIDP oxidation by singlet oxygen. The rate constant for the oxidation of BIDP by $^1O_2$ (k_{OX}) may be estimated from these experiments by considering the deactivation channels of $^1O_2$, Eqs. (7) and (8).

The quantum yield of oxidation in MeCN is given by

$$\varphi^{CN}_{OX} = \frac{k^{CN}_{OX}[P]^{CN}_0}{k^{CN}_{OX}[P]^{CN}_0 + k^{CN}_D} \tag{9}$$

and a corresponding equation holds for hexane. The ratio of the quantum yields is then given by:

$$\frac{\varphi^{CN}_{OX}}{\varphi^{H}_{OX}} = 12.5 = \frac{k^{CN}_{OX}[P]^{CN}_0}{k^{H}_{OX}[P]^{H}_0}\left\{\frac{k^{H}_{OX}[P]^{H}_0 + k^{H}_D}{k^{CN}_{OX}[P]^{CN}_0 + k^{CN}_D}\right\} \tag{10}$$

The only unknown quantity in this equation is k^{H}_{OX}, the rate constant for oxidation of BIDP by $^1O_2$ in hexane. Using the experimental value for the ratio (12.5) and $k^{CN}_{OX} = 1 \times 10^9\ M^{-1}\ s^{-1}$ and $[P]_0$ concentrations in MeCN and hexane (4×10^{-5} M and 3×10^{-5} M, respectively) we derive $k^{H}_{OX} = 7 \times 10^7\ M^{-1}\ s^{-1}$, namely 14 times smaller than in MeCN.

The major assumption of the above kinetic scheme is that the sensitized photo-oxidation is the only reactive channel, and there are no additional reactions between BIDP and BP. In a control experiment, the same reaction was carried out in nitrogen saturated solutions. A weak new band appearing at 325 nm indicated some photochemistry between BIDP and benzophenone in nitrogen saturated hexane solution whereas in MeCN nitrogen saturated solutions a similar reaction was not observed. However the photo-reaction between benzophenone and BIDP in nitrogen saturated hexane solution is not important under the conditions of the photo-sensitized oxidation experiments as the addition of molecular oxygen appears to block this reaction channel: no additional bands are observed around 325 nm during sensitized photo-oxidation. This can be rationalized by considering that the concentration ratio of oxygen to BIDP in these experiments is about 100. Assuming that the second order rate constants for the reaction of triplet benzophenone with both compounds (oxygen and BIDP) are similar, the pseudo-first order rate constant of the reaction with oxygen must be two orders of magnitude higher than that of BIDP.

4. Discussion

The main experimental results of this work are summarized in Tables 1–3. It was found that the oxidation quantum yield is higher in polar solvents than in non-polar ones; moreover, the quantum yields in the different alkanes are the same within experimental error. Therefore, in the following discussion data obtained in experiments with MCH and hexane are considered to be equivalent. The solvent effect was larger using Filter A, which allowed irradiation down to 320 nm than in the red-transmitting Filter B and C. In view of the photo-sensitization experiments, the increased quantum yield may be due to the production of carbonyl compounds in the photo-oxidation. They absorb in the UV (within the transmission window of Filter A) and may sensitize the formation of $^1O_2$ in a mechanism similar to benzophenone, leading to a fictitious increase in the apparent quantum yield. At this time the nature of the products has not been elucidated yet, therefore a discussion of this apparent violation of Kasha's rule [13] is deferred to the future. The following analysis will be based of data obtained with Filters B or C, for which no such complications are anticipated as the products do not absorb in their transmission range.

4.1. A proposed mechanism

The following heuristic mechanism may account for the self-sensitized photo-oxidation experimental data (P stands for the dihydropyridine derivative):

$$P(S_0) + h\nu \rightarrow P(S^*) \tag{11}$$

$$P(S^*) \rightarrow P(S_0) + h\nu' \quad \left(k^{0}_{F}\right) \tag{12}$$

$$P(S^*) \rightarrow P(S_0) \quad (k_{IC}) \tag{13}$$

$$P(S^*) \rightarrow P(T^*) \quad (k_{ISC}) \tag{14}$$

$$P(T^*) \rightarrow P(S_0) \quad (k_{ISC} + k_P) \tag{15}$$

$$P(T^*) + Q \rightarrow P(S_0) + Q^* \quad (k_{Q,T}) \tag{16}$$

$$P(T^*) + O_2 \rightarrow P(S_0) + {}^1O_2 \quad (k_{ET}) \tag{17}$$

$${}^1O_2 \rightarrow {}^3O_2 \quad \left(k_{ISC''} + k_{P,O}\right) \tag{18}$$

$$S + {}^1O_2 \rightarrow \text{products} \quad \left(k_{OX,S}\right) \tag{19}$$

$$P + {}^1O_2 \rightarrow \text{oxidation products} \quad (k_{OX}) \tag{20}$$

Step (11) is excitation to the first excited singlet state, a process that may involve initial excitation of higher excited states. Preliminary ultrafast experiments [1,14] show that the molecule stays on the excited singlet manifold less than a picosecond, so that for all practical purposes initial excitation may be assumed to populate S_1 on a time scale shorter than all subsequent processes. Processes (12)–(14) depopulate S_1; the main deactivation process for the S_1 singlet state (denoted as P(S*)) is internal conversion with a rate constant k_{IC} of the order of $10^{12}\ s^{-1}$ (the estimate is based on the lack of fluorescence (or very small quantum yield) [15] and the preliminary ultrafast experiments [14]). The experimental oscillator strength of the S_0–S_1 transition is 0.38 in MeCN; this translates to a radiative rate constant k^0 of $1.3 \times 10^8\ s^{-1}$ in MeCN. The intersystem crossing rate constant k_{ISC} is expected to be of the same order of magnitude, as for other substituted olefins [16] (see below for more exact estimates for k_{ISC} in MeCN and MCH solutions). Processes 16 thru 18 depopulate T_1; $k_{ISC''} + k_p$ represents the sum of the intersystem rate constant leading from T_1 to S_0 and the phosphorescence rate constants, $k_{Q,T}$ is a quenching rate constant of the triplet by the solvent (and possibly impurities) and k_{ET} is the rate constant of energy transfer to form singlet oxygen. Processes (18)–(20) represent the decay of $^1O_2$, by intersystem crossing or radiation (18), by interaction with the solvent or impurities (19) and by reaction with the ground state P (20). The latter process is used to follow the rate of the overall reaction, which leads to oxidation of P and bleaching of the color.

According to this mechanism, the yields for triplet formation, singlet O_2 formation and substrate oxidation are given by Eqs. (21)–(23), respectively.

$$\phi(T) = \frac{k_{ISC}}{k_{ISC} + k_f^0 + k_{IC}} \tag{21}$$

$$\phi(^1O_2) = \frac{k_{ET}[O_2]}{k_{ET}[O_2] + k_{ISC''} + k_P + k_{Q,T}[Q]} \tag{22}$$

$$\phi(OX) = \frac{k_{OX}[P]}{k_{OX}[P] + k_{OX,S}[S] + k_{IISC''} + k_{P,O}} \tag{23}$$

The overall oxidation yield $\Phi_{TOT}(OX)$, for which experimental results were reported in Tables 1 and 2 is given by

$$\phi_{TOT}(OX) = \phi(T)\phi(^1O_2)\phi(OX) \tag{24}$$

From the available experimental data, $k_{IC} \gg k_{ISC} + k_f^0$; therefore, $\phi(T)$ can be approximated by k_{ISC}/k_{IC}. The ultrafast experiments [14] that show a sub-picosecond decay of stimulated emission lend support to this approximation. k_{ET} is of the order [17,18] of $5 \times 10^9\ M^{-1}\ s^{-1}$, and the concentration of molecular oxygen in the air-saturated experiments was about 2×10^{-3} M [19]; therefore k_{ET} $[O_2]$ equals about $10^7\ s^{-1}$. The lifetime of the lowest triplet state of olefins in the absence of molecular oxygen is determined by the other three terms in the denominator of Eq. (22). In olefins and polyenes it is of the order of 50 μs [20], i.e. the other terms together are $2 \times 10^4\ s^{-1}$. Therefore, $\phi(^1O_2)$ is about 1.0, independent of the solvent, as found in similar systems [17,18]. k_{OX} is $10^9\ M^{-1}\ s^{-1}$ and $7 \times 10^7\ M^{-1}\ s^{-1}$ in MeCN and hexane, respectively (Section 3.3). It may be assumed that k_{OX} in MCH is similar to that in hexane as the lifetime of $^1O_2$ in MCH is essentially identical to that in hexane [21].

Experimentally $\Phi_{TOT}(OX)$ in MeCN is four times larger than in MCH (Table 1 Filter B).

Eq. (24) can be used to derive the relative efficiencies for intersystem crossing in MeCN and MCH.

From the benzophenone sensitized experiments:

$$\frac{\{\phi(OX)\}_{MeCN}}{\{\phi(OX)\}_{HEX}} = 12.5$$

Assuming that $\phi(^1O_2)$ is equal in the two solvents [12,22], it follows that.

$$\frac{\{\phi(T)\}_{MeCN}}{\{\phi(T)_{MCH}\}} = 0.32$$

Thus, the yield of the triplet is about three times larger in MCH than in MeCN.

Using Eqs. (7) and (8) and the numerical data, $\phi(OX)$, the quantum yield for oxidation of BIDP by $^1O_2$ can be estimated, assuming that k_D is given by τ_0^{-1}, where τ_0 is the lifetime of $^1O_2$ in the solvent. With [BIDP] = 4×10^{-5} M, one gets that $\phi(OX)$ equals 0.76 and 0.061 in MeCN and hexane, respectively.

These figures, together with the overall photo-oxidation quantum yields $\Phi(OX)$ from Table 1 can be used to derive the quantum yields for triplet formation in BIDP, $\phi(T)$ using Eq. (23) and $\phi(^1O_2) = 1.0$ for both MeCN and MCH. The derived values are, $\Phi(T)_{MeCN} + 1.1 \times 10^{-4}$ and $\Phi(T)_{MCN} = 3.4 \times 10^{-4}$.

It follows that intersystem crossing is a minor channel in the decay of BIDP singlet in both solvents considering that all electronically excited molecules end up in the ground state. Since $k_{IC} \gg k_{ISC}$ and also $k_{IC} \gg k_f^0$, the quantum yields of triplet formation $\phi(T)$ and of fluorescence, ϕ_f, can be approximated by Eqs. (25) and (26), respectively:

$$\phi(T) = \frac{k_{ISC}}{k_{IC}} \tag{25}$$

$$\phi = \frac{k_f^0}{k_{IC}} \tag{26}$$

From Eq. (25), k_{ISC} may be estimated if k_{IC}, the dominant decay rate constant of the S_1 state of BIDP, is known. From the measured oscillator strength and fluorescence quantum yield we estimate $3 \times 10^{11}\ s^{-1}$ and $2 \times 10^{12}\ s^{-1}$ for k_{IC} in MeCN and MCH, respectively [15]. These values lead to $k_{ISC} = 3.3 \times 10^7\ s^{-1}$ and $3.4 \times 10^8\ s^{-1}$ for MeCN and MCH, respectively. The magnitude for MeCN is in agreement with the expected value for an olefin, whereas for MCH a rather high rate constant is found. It has been recently suggested that the intersystem crossing probability is enhanced near a conical intersection [23]. It was shown that at a S_1/S_0 conical intersection, in many molecules the T_1 state is degenerate with the two singlet states. Moreover, the spin–orbit coupling matrix element at this geometry is necessarily large, so that intersystem crossing can be quite efficient.

The faster rate obtained in a non-polar is in accord with the existence of a conical intersection in non-polar solvents. Table 4

Table 4
Parameters derived for the photo-oxidation of BIDP

	MeCN	Non-polar
k_{IC}	3×10^{11} s^{-1}	2×10^{12} s^{-1}
k_{ISC}	3.3×10^{7} s^{-1}	3.4×10^{8} s^{-1}
k_{OX}	10^{9} M^{-1} s^{-1}	7×10^{7} M^{-1} s^{-1}
ϕ_{OX}[a]	0.76	0.061
ϕ_{T}[b]	1.1×10^{-4}	3.4×10^{-4}

Non-polar solvents are hexane and MCH, the rate constants and quantum yields are assumed to be equal for these two solvents.

[a] At [BIDP] = 5×10^{-5} M.

[b] At room temperature.

summarizes the numerical parameters derived from the proposed mechanism.

4.2. Justification of the mechanism

The quenching experiments are consistent with the assumption that the quenched species is $^1O_2$. Table 3 summarizes the experimental results. The quenching rate constants calculated using $^1O_2$ lifetime data in the various solvents are of the order of 10^9 and 3×10^8 for TMA and NaN_3 in MeCN, respectively and 2×10^4 M^{-1} s^{-1} for PP, in hexane and ethylacetate. These values agree reasonably well with known rate constants for quenching of $^1O_2$: 3×10^8, 4.8×10^9 and 2×10^4 M^{-1} s^{-1} for TEA (triethylamine) in MeCN [24,25], NaN_3 in MeCN [26] and dimethylbutadiene in $CHCl_3$ [27], respectively (we are not aware of a measurement for a diene in hexane or ethylacetate). Especially notable is the much smaller value for PP compared to the other two quenchers. The higher literature value reported for NaN_3 quenching in MeCN (Ref. [26]) is somewhat out of line with data measured for this quencher in water [28], methanol [29] and ethanol [11]—the rate constants for all three are smaller by a factor of 10. We therefore tend to believe that our measured k_Q is reasonable. The observed Stern–Volmer rate constants are not compatible with quenching of either the triplet or singlet excited states of the compounds (see last column of Table 3).

4.3. Other possible mechanisms

The proposed mechanism appears to be consistent with the experimental data, but its validity must be checked by further independent experiments. An obvious one would be the direct observation of the triplet by triplet–triplet absorption or by phosphorescence. Attempts to detect the triplet at room temperature led to negative results; experiments at lower temperatures may be more fruitful and are being planned.

The ultra-short lifetime of the singlet might appear at first sight to preclude a reaction of the molecule in its excited singlet state with molecular oxygen. However if a diffusion controlled rate constant is assumed (about 10^{10} M^{-1} s^{-1}), the concentration of O_2 in air-saturated solutions of about 2×10^{-3} M in organic solvents [19] would yield a pseudo-first-order rate constant of 2×10^7 s^{-1}, and a quantum yield of the order of 10^{-5} to 10^{-6}. These yields are somewhat smaller than the measured ones, so that the mechanism of the reaction is expected to involve longer-lived reactive specie, such as the triplet. Nonetheless, this option must also be considered in more detail.

5. Concluding remarks

The room temperature self-sensitized photo-oxidation of BIDP and BIMDP proceeds cleanly and irreversibly, though with a rather small quantum efficiency (10^{-5} to 10^{-3}). The small efficiency is consistent with the very short lifetime of the lowest singlet state (~10^{-12} s) deduced from the absence of fluorescence at room temperature. The quantum yields are solvent dependent, the reaction being more efficient in polar solvents than in non-polar ones. Quenching experiments suggest that the oxidation is due to singlet oxygen, formed in turn by triplet sensitization. The solvent effect is mainly due to the faster reaction of singlet oxygen with the substrates in polar solvents. Ultrafast experiments [14] (to be reported separately) confirm the proposed picosecond decay of the initially excited singlet state, which is assigned to rapid internal conversion (IC). According to a mechanism proposed to explain the observed data the formation of a triplet state by intersystem crossing (ISC) whose rate constant is ~10^{-3}–10^{-4} smaller than that of IC accounts for the small observed overall quantum yield.

Acknowledgments

We thank Dr. L. Lustres and Prof. N. Ernsting for carrying out the ultrafast experiments mentioned in the manuscript and for most useful discussions. We are grateful to Prof. Peter Ogilby for a discussion of the $^1O_2$ quenching mode and thank Prof. Israel Agranat for some most enlightening discussions. We are indebted to Anat Kahan of our laboratory for helping with the measurements and the calculations and many discussions. The Minerva Farkas Center for Light Induced Processes is supported by the Minerva Gesellschaft mbH.

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