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Journal of Photochemistry and Photobiology A: Chemistry 187 (2007) 105–112

Journal of Photochemistry and Photobiology A:Chemistry

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Oxygen uptake upon photolysis of 3-benzoylpyridine and 3,3′-dipyridylketone in air-saturated aqueous solution in the presence of formate, ascorbic acid, alcohols and amines

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Received 24 August 2006; accepted 30 September 2006

Abstract

The effects of oxygen in the photolysis of 3-benzoylpyridine (3-By) and 3,3′-dipyridylketone (3,3′-Dy) in aqueous solution were studied in the presence of appropriate donors: formate, ascorbic acid, amines, e.g. triethylamine and alcohols, e.g. 2-propanol. The quantum yield of oxygen uptake (Φ_{-O_2}) increases with the donor concentration, approaching $\Phi_{-O_2} = 0.6$, e.g. for ascorbic acid or triethylamine (>1 mM) and 2-propanol (>0.1 M). Quenching of the triplet state by the donor and subsequent reaction of both acceptor and donor radicals with oxygen leads to formation of hydrogen peroxide. The radicals of the mono- and dipyridylketones terminate into an “iso”benzpinacol-type product. This reaction is minor and major in the presence and absence of air, respectively. For *N*-methylphthalimide, a related heterocyclic sensitizer, the mechanism of oxygen uptake is the same: oxidation of the donor and conversion of oxygen via the hydroperoxyl radical into H_2O_2, but the Φ_{-O_2} values are smaller. The relevant properties of donors, the radicals involved and the pH and concentration dependences are discussed.

Keywords: Superoxide radical; Triplet; Photooxidation; Photoreduction; Electron transfer

1. Introduction

The photodynamic action of a sensitizer generally refers to electron transfer (type I) yielding hydroperoxyl/superoxide ion radicals ($HO_2^{\bullet}/O_2^{\bullet-}$) and to energy transfer (type II) yielding singlet molecular oxygen: $O_2(^1\Delta_g)$ [1–7]. Compilations of the latter quantum yields (Φ_Δ) from biologically relevant molecules are available [6,7]. In addition, the superoxide radical can be generated, for Rose Bengal in aqueous solution the quantum yield is small (0.02–0.2) with respect to $\Phi_\Delta = 0.76–0.86$ [3,5]. Related systems utilize methylene blue [8], eosin [9] and flavins [10]. For riboflavin the quantum yields of formation of the $HO_2^{\bullet}/O_2^{\bullet-}$ radical and of $O_2(^1\Delta_g)$ are 0.01 and 0.5, respectively [10a]. Vitamin C (ascorbic acid) is known to enhance the quantum yield of oxygen uptake (Φ_{-O_2}) as a measure of the conversion of oxygen via the superoxide radical into hydrogen peroxide [8]. The kinetic features of the $HO_2^{\bullet}/O_2^{\bullet-}$ radical in aqueous solution are known from radiolysis [11–14].

Recently, the photoinduced O_2 uptake/consumption was studied in air-saturated mixtures of water with acetonitrile in the presence of appropriate donors for anthraquinone and ketones, such as acetophenone, benzophenone (Bp), 4-carboxybenzophenone and benzil [15,16]. Some of these ketones have been intensively investigated by photochemical means [17–30]. It is interesting to question the role and subsequent fate of oxygen in the photochemistry of other sensitizers, e.g. specific heteroaromatic ketones. The photolytic properties of benzoylpyridines (Bys) and dipyridylketones (Dys), which are heterocyclic homologues of Bp, and a few related arylpyridylketones have been reported [31–35]. The position of the nitrogen is a major factor in the photochemistry since for 2-By and 2,2′-Dy cyclization has been reported [32]. The characteristic features of the ketyl radicals in aqueous solution are also known, e.g. $pK_a = 9.2$ for 3-By [36].

Φ_{-O_2} values are presented in this work for 3-By, 3,3′-Dy and *N*-methylphthalimide (Me-Pi) in the presence of H-atom donors, such as 2-propanol, methanol or formate. Moreover, ascorbic acid and several amines, e.g. triethylamine (TEA), diethylamine (DEA), *N*,*N*-diethylhydroxylamine (DHA) or ethylenediaminetetraacetate (EDTA), were used as electron

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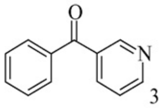
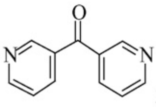
doi:10.1016/j.jphotochem.2006.09.018

donors. Me-Pi is a frequently used photosensitizer with regards to oxidative cyclization [37–40]. UV irradiation of the three model compounds in air-saturated aqueous solution in the presence of a donor leads to the conversion of O_2 into hydrogen peroxide. The results are compared with those from quenching of the ketone triplet state by these electron or H-atom donating additives and the radicals by oxygen using time-resolved UV–vis spectroscopy at 248 and 308 nm. Oxygen acts by quenching of the triplet state and scavenging of the radicals derived from both the donors and the ketones.


3-By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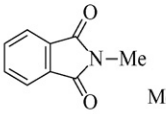
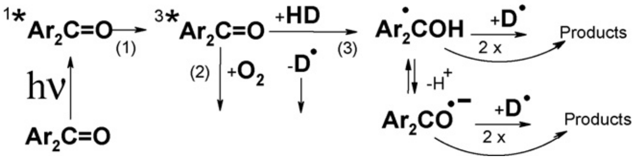

Me-P

2. Experimental details

3,3′-Dy was prepared by Aldo Romani and a gift from Professor G. Favaro from Perugia, the other compounds (EGA, Sigma) and the solvents (Merck) are commercially available and were checked for impurities and used as received; DEA and TEA were purified by distillation. Water was from a millipore milliQ system. The UV/vis absorption spectra were monitored on a diode array spectrophotometer (HP, 8453). For photoconversion the 280, 313 or 366 nm lines of a 1000 W Hg-Xe lamp and a monochromator were used, pathlength 1 cm. The solutions in the presence of ascorbic acid were at pH 2–3. For the TEA or DHA cases the typical pH was 12–13. The ion concentration was kept as low as possible, e.g. pH was close to 7 in the presence of alcohols or formate, albeit phosphate buffer in these cases appeared to have no effect on Φ_{-O_2}. It should be noted that traces of metals in buffers were claimed to affect the formation of hydrogen peroxide in the case of riboflavin and ascorbic acid [10b], but here Φ_{-O_2} was found to be unchanged for 3-By in the presence of 1 mM ascorbic acid and 10 mM phosphate buffer at pH 7. The oxygen concentration was determined by a Clark electrode (Hansatech). The oxygen concentration under air at 24 °C is taken as 0.27 mM and it generally decreases upon photolysis in a specific way, mostly with a linear portion. The relative yield of oxygen consumption was determined from the slope versus irradiation time. As actinometers at 280 and 313/366 nm uridine and aberchrome 540 were used, respectively [41]. The experimental error in the quantum yield determination is ±15% for Φ_{-O_2} larger than 0.1 and ±30% for the smaller values. Excimer lasers (Lambda Physik, pulse width of 20 ns and energy <100 mJ) were used for excitation at 308 and 248 nm (EMG 200, EMG 210 MSC). The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling. The molar absorption coefficients for the triplet of 3-By and 3,3′-Dy are like Bp: $\varepsilon_{525} = 6 \times 10^3\ M^{-1}\ cm^{-1}$ [30]. The values of the radicals are similar, based on $\varepsilon_{525} = 5.6 \times 10^3\ M^{-1}\ cm^{-1}$ for $Ar_2{}^{\bullet}COH$ of 4-By and $\varepsilon_{605} = 5.6 \times 10^3\ M^{-1}\ cm^{-1}$ for $Ar_2CO^{\bullet-}$ [36]. The k_3 values, due to the spectral similarities of triplet and radical at pH <12, were taken at pH 12.5–13; the experimental error (±30%) is larger than for ketones. The measurements refer to 24 °C.



Scheme 1.

3. Results and discussion

3.1. Initial photoreactions of mono- and dipyridylketone

Aromatic ketones containing phenyl or pyridyl rings have generally a high quantum yield of intersystem crossing (Φ_{isc}) [28,30] and a high Φ_{Δ} [6,7]. The photoreactions of the mono- and dipyridylketones start from the triplet state ($^{3*}Ar_2CO$) after intersystem crossing (Scheme 1). The triplet lifetime (τ_T) in argon-saturated aqueous solution at room temperature is 6–8 µs and up to 12 µs, when the substrate concentration and the laser intensity are low enough. A literature value for 3,3′-Dy in acetonitrile is $\tau_T = 18$ µs [33]. The lifetime in air-saturated solution is shorter, e.g. $\tau_T = 2.1$ and 2.9 µs for 3-By and 3,3′-Dy, respectively. The rate constant for quenching of the triplet state by oxygen is $k_2 = 2.5 \times 10^9\ M^{-1}\ s^{-1}$ for 3,3′-Dy in acetonitrile [33] and k_2 is similar in water. For various ketones in acetonitrile–water (1:1, vol) $k_2 = (1–12) \times 10^9\ M^{-1}\ s^{-1}$ [15]. Quenching reaction (2) yields singlet molecular oxygen [6,7]. Practically no $O_2(^1\Delta_g)$-mediated product is expected in the absence of macromolecules since the ketone concentration is moderate and the lifetime of $O_2(^1\Delta_g)$ in aqueous solution is as short as a few µs. Triplet quenching by oxygen competes with quenching by the respective donor, reaction (3).

$$^{3*}Ar_2C = O + DH \rightarrow Ar_2{}^{\bullet}COH/Ar_2CO^{\bullet-} + D^{\bullet}/HD^{\bullet+} \quad (3)$$

Four donor types were chosen for irradiation of the ketone/water/air system: formate, ascorbic acid as unique radical scavenger, 2-propanol as example of a reactive alcohol and aliphatic amines. Photoreduction yields the $Ar_2{}^{\bullet}COH/Ar_2CO^{\bullet-}$

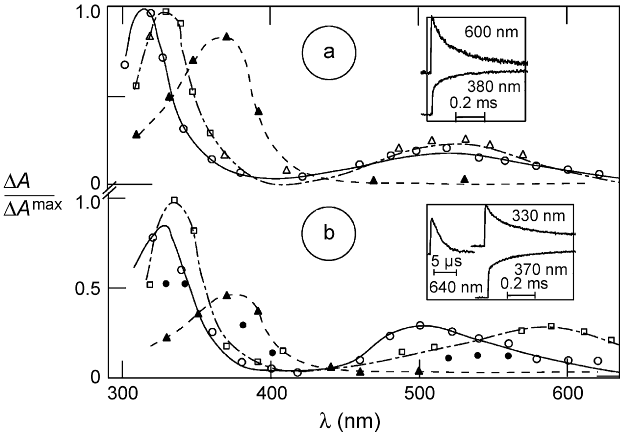


Fig. 1. Transient absorption spectra of 3-By in argon-saturated aqueous solution at (a) pH 7 and (b) pH 13 in the presence of 10 mM fomate at 20 ns (○), 1 µs (△), 10 µs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics as indicated.

Table 1
Rate constants for quenching (10^9 M^{-1} s^{-1}) by donors[a]

Donor	3-By	3,3′-Dy	Me-Pi	Bp[b]
Formate	0.2	0.1	<0.002	0.10
Ascorbic acid	2	2	1	1.2
tert-Butanol	0.001	0.001	<0.001	
2-Propanol	0.04	0.02	0.001	0.002
TEA	2	2[c]	1.2	1.6
EDTA	2	2	2	1.5

[a] In argon-saturated aqueous solution.
[b] Taken from Ref. [15].
[c] Same value for DHA.

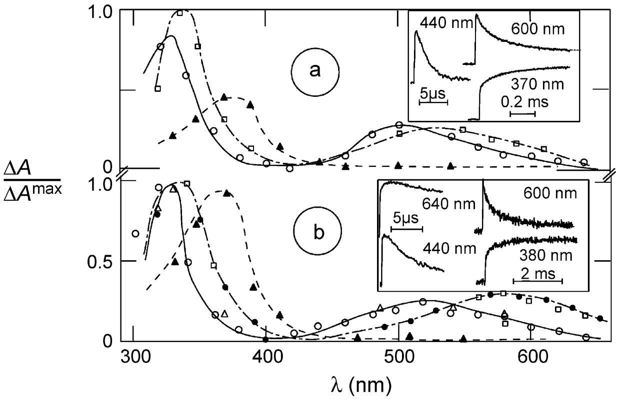


Fig. 2. Transient absorption spectra of 3-By in argon-saturated aqueous solution at (a) pH 7 and (b) pH 13 in the presence of 0.1 M 3-propanol at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 248 nm pulse; insets: kinetics as indicated.

radical as observable secondary transient, at least under argon. Transient absorption spectra and kinetics upon pulsed 248 nm photolysis are shown for 3-By in argon-saturated aqueous formate solution at pH 7 and 13 (Fig. 1a and b). The spectra have the two characteristic maxima around 310 and 500 nm for the triplet state. The spectra of the (di)pyridylketone radical and triplet state are rather similar. The rate constant k_3 was determined from plots of $1/\tau_T$ versus the donor concentration (Table 1). Different to Bp, where decay of the radical yields mainly the ketone, the results in Fig. 1a and b show the conversion into a photoproduct with maximum at 360 nm. The transient absorption spectra in presence of 2-propanol and TEA reveal the same 360-nm product (Figs. 2 and 3). This is in agreement with the literature, as the photoproduct of 3-By in oxygen-free 2-propanol–water has a characteristic absorption band centered at 360 nm [34].

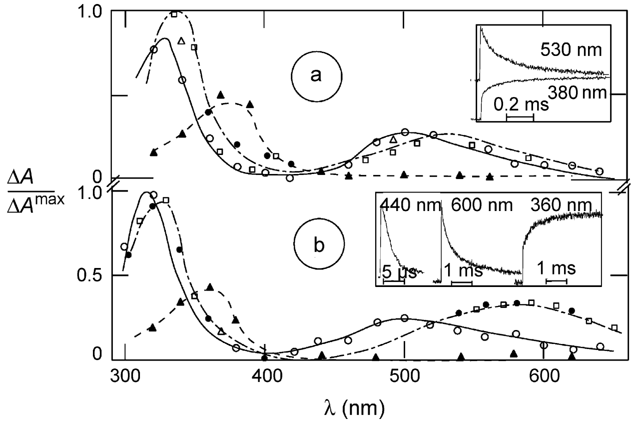
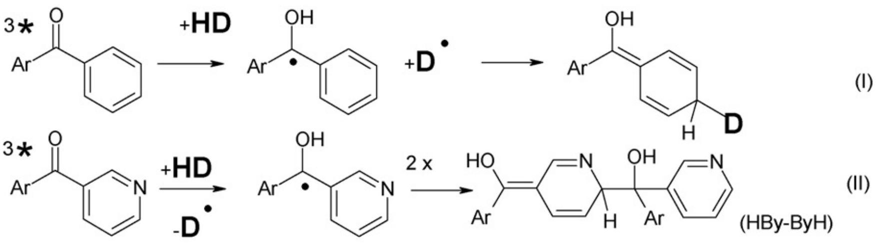


Fig. 3. Transient absorption spectra of 3-By in argon-saturated water at (a) pH 7 and (b) pH 13 in the presence of 1 mM TEA at 20 ns (○), 1 μs (Δ), 10 μs (□), 0.1 ms (●) and 1 ms (▲) after the 308 nm pulse; insets: kinetics as indicated.

3.2. Photoproducts of 3-benzoylpyridine and 3,3′-dipyridylketone

The observed 360-nm product is a so-called light absorbing transient (LAT). LATs are quasi-stable intermediates resulting from radical termination. Involvement of LATs in the photoreduction of Bp by alcohols, benzhydrol or other H-donating agents has been intensively investigated [17–25]. The LAT formation by radical termination via cross-coupling, reaction (I) in Scheme 2, is generally accepted [22–25]. A LAT yield of 20% for Bp/2-propanol in acetonitrile was ascribed to competition kinetics, taking $k_q = 0.5 \times 10^8$ M^{-1} s^{-1} for self-reaction of the ketyl radicals, $k_q = 11 \times 10^8$ M^{-1} s^{-1} for self-reaction of the 2-hydroxy-propyl radicals and $k_q = 9 \times 10^8$ M^{-1} s^{-1} for cross-reaction of the two radicals [25].

For the 3-By/2-propanol system in deoxygenated aqueous solution Albini et al. [34] have assigned the LAT-photoproduct to an "iso"benzpinacol-type structure (denoted here as HBy-ByH). They proposed a slightly different mechanism, where the radical termination takes place via self-reaction (II). Here, the changes are shown for 3-By in argon-saturated aqueous solution in the presence of formate, ascorbic acid, 2-propanol and TEA (Fig. 4a–d). The spectra are not indicative for the kind of donor, supporting the mechanism of radical self-coupling. For 3,3′-Dy the four donor types can also be applied, an example is shown in Fig. 5 for 2-propanol. The results reveal a similar photoinduced band centered at 360 nm and likewise the self-coupling mechanism is proposed. Photolysis of 3-By and 3,3′-Dy in the presence



Scheme 2.

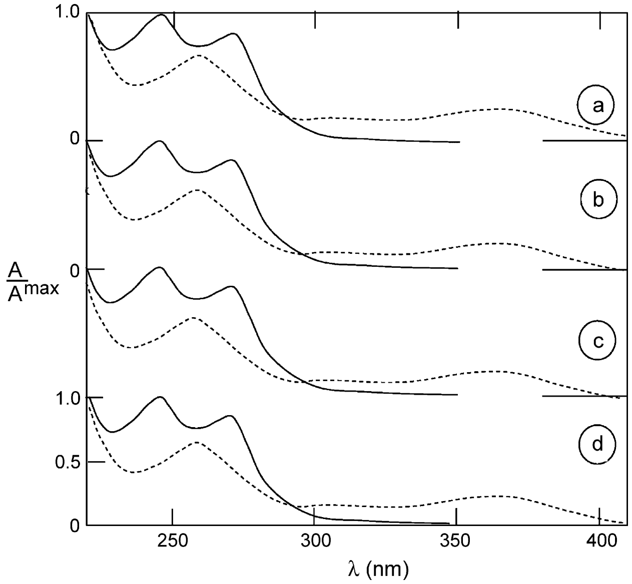


Fig. 4. Absorption spectra of 3-By in argon-saturated aqueous solution prior to (full line) and after irradiation at 254 nm (broken) in the presence of (a) 0.1 M formate, (b) 1 M 2-propanol, (c) 1 mM ascorbic acid and (d) 1 mM TEA.

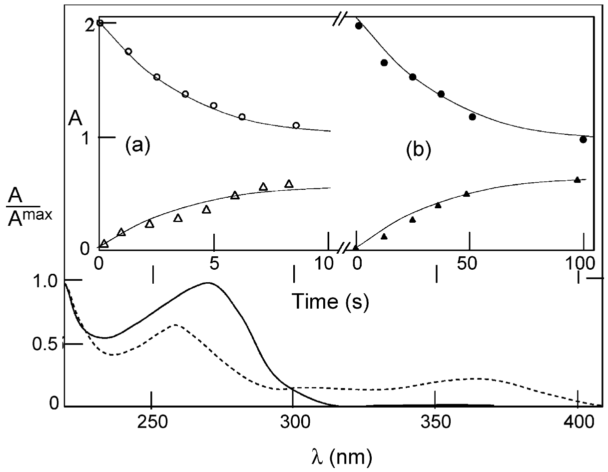
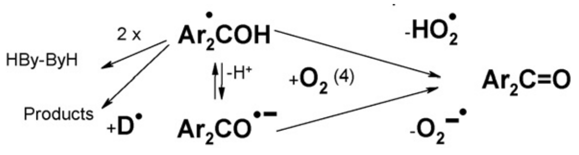


Fig. 5. Absorption spectra of 3,3′-Dy in argon-saturated aqueous solution prior to (full line) and after 254 nm irradiation (broken) in the presence of 0.1 M 2-propanol; insets: time dependence at 270 nm (cirlces) and 360 nm (triangles) (a) argon- and (b) air-saturated.

of donors leads to a quantum yield ($\Phi_{-\mathrm{py}}$) of decomposition of $\Phi_{-\mathrm{py}} = 0.1$–1 (Table 2).

LAT formation requires the exclusion of oxygen [17–25,34]. Such a photoprocess in air-saturated aqueous solution is now presented for the first time (to our knowledge), see Scheme 3. Formation of the 360 nm band under air is observable (inset Fig. 5 and Table 2), but $\Phi_{-\mathrm{py}}$ is much smaller (ca. 10-fold) than in the oxygen-free case. For Bp it is known that oxygen addition (after oxygen-free LAT formation) causes splitting into Bp and the alcohol [17–25]. In contrast, no oxygen-mediated splitting effect was found for the two pyridylketones.



Scheme 3.

Table 2
Quantum yield of decomposition ($\Phi_{-\mathrm{py}}$) in the presence of donors[a]

Donor	3-By argon	3-By air	3,3′-Dy argon	3,3′-Dy air
None	<0.01	<0.01	<0.003	<0.01
Formate	0.9	0.06	0.9	0.1
Ascorbic acid	0.7	0.08		
2-Propanol	0.9	0.05	0.9	0.1
TEA	0.4 (0.8)[b]	0.06	0.8	0.08
EDTA	0.9	0.1	0.6	<0.1

[a] In aqueous solution, using concentration of 0.001, 0.01, 0.1 and 1 M, for ascorbic acid, amines, formate and 2-propanol, respectively, $\lambda_{\mathrm{irr}} = 254$ nm.

[b] For DHA.

3.3. Photoreactions of (di)pyridylketones with oxygen and formate

Upon UV irradiation at 280, 313 or 366 nm of ketones in air-saturated aqueous solution, the voltage of the Clark electrode as a measure of the O_2 concentration decreases with time. Examples of the electrode signal versus time in the presence of formate are shown in Fig. 6 (inset), $\lambda_{\mathrm{irr}} = 313$ nm. The plots of the oxygen concentration versus irradiation time are initially downward curved, reach a major linear part and level off. The slope of this is taken to be proportional to the quantum yield of the O_2 consumption. The $\Phi_{-\mathrm{O_2}}$ values increase with [formate], as shown in Fig. 6 for 3-By. $\Phi_{-\mathrm{O_2}}$ is 0.6 for irradiation of 3-By and 3,3′-Dy at 313 nm using 0.1–1 M formate (Table 3). The k_3 values are $1 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ (Table 1) which is larger than for Bp [15]. The half-concentrations, $[\text{formate}]_{1/2}$, i.e. the donor concentrations for 50% of the maximum $\Phi_{-\mathrm{O_2}}$ values, are 8 and 6 mM for 3,3′-Dy and 3-By, respectively (Table 4). The reactions of the formate ion with a triplet state of an acceptor have been stud-

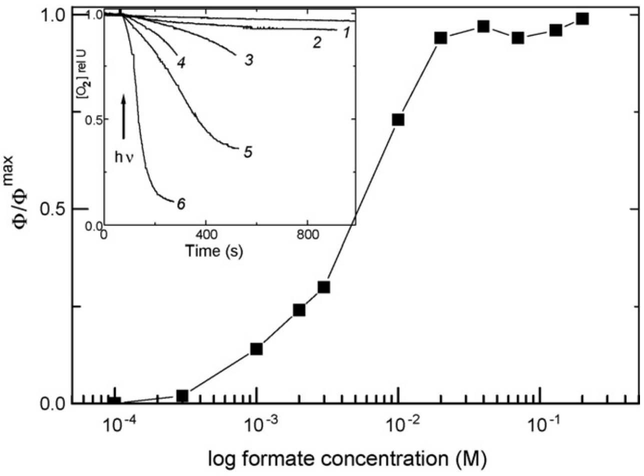


Fig. 6. Semilogarithmic plot of the quantum yield $\Phi_{-\mathrm{O_2}}$• ($\lambda_{\mathrm{irr}} = 313$ nm) as a function of the formate concentration for 3-By in air-saturated aqueous solution. pH 7; insets: plots of the O_2 concentration vs. irradiation time in the presence of formate: 0, 0.1, 0.3, 1, 3 and 30 mM, 1–6, respectively.

Table 3
Quantum yield of oxygen uptake (Φ_{-O_2}) in the presence of donors[a]

Donor	3-By	3,3′-Dy	Me-Pi	Bp[b]
None	<0.01	<0.01	<0.003	<0.01
Formate	0.6	0.6	<0.01	0.5
Ascorbic acid	0.5 (0.4)[c]	0.7	0.23	0.7
tert-Butanol	0.08	0.1		
2-Propanol	0.5 [0.4][d]	0.5	0.01	0.9
TEA	0.4	0.5	0.1	0.8
DHA	0.4	0.3	0.2	
EDTA	0.3	0.4	0.2	0.8

[a] In air-saturated aqueous solution, donor concentrations as in Table 2, $\lambda_{irr} = 313$ nm.

[b] Taken from Ref. [15].

[c] Using $\lambda_{irr} = 280$ nm.

[d] Using $\lambda_{irr} = 366$ nm.

Table 4
Experimental values of half-concentration (mM) for Φ_{-O_2} in the presence of donors[a]

	3-By	3,3′-Dy	Me-Pi	Bp[b]
$[\text{Formate}]_{1/2}$	6 (5)[c]	8		20 (17)
$[\text{Ascorbic acid}]_{1/2}$	0.4	0.2	2	2 (1.4)
$[\text{2-Propanol}]_{1/2}$	60	50	>1000	900 (800)
$[\text{TEA}]_{1/2}$	<0.3 (0.2)	0.2		<2 (1.0)
$[\text{DHA}]_{1/2}$	0.5		2	
$[\text{EDTA}]_{1/2}$	0.5		1	

[a] In air-saturated aqueous solution, $\lambda_{irr} = 313$ nm.

[b] Taken from Ref. [15].

[c] Values in parentheses were calculated using $\tau_T = 2$ μs for 3-By.

ied for 4-carboxybenzophenone and Bp-4-sulfonate [27]. The reactions of formate with the ketone triplets are illustrated in Schemes 4 and 5. Quenching occurs via H-atom transfer (3a), whereby the acceptor (ketyl) radical is formed which is converted back into the ketone via reaction (4). The lifetime of the ketyl radical under air was found to be not longer than τ_T, i.e. $k_4 > 1 \times 10^8$ M^{-1} s^{-1}.

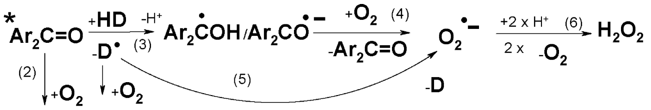
$$Ar_2{}^{\bullet}COH + O_2 \rightarrow Ar_2C{=}O + HO_2{}^{\bullet}/(O_2{}^{\bullet -} + H^+) \quad (4)$$

$$CO_2{}^{\bullet -} + O_2 \rightarrow CO_2 + O_2{}^{\bullet -} \quad (5a)$$

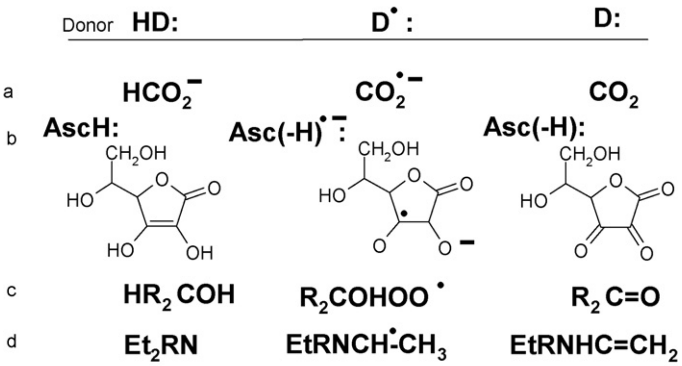
$$2 \times HO_2{}^{\bullet}/(O_2{}^{\bullet -} + H^+) \rightarrow H_2O_2 + O_2 \quad (6)$$

$$HCO_2{}^- + O_2{}^{\bullet -} + H^+ \rightarrow CO_2{}^{\bullet -} + H_2O_2 \quad (7a)$$

Reaction (5a) occurs with $k_5 = 4 \times 10^9$ M^{-1} s^{-1} [29] and eventually oxygen is converted via the $HO_2{}^{\bullet}/O_2{}^{\bullet -}$ radical into H_2O_2. The kinetics of dismutation of superoxide radicals have characteristic pH dependence [13]. One step for H_2O_2 formation is reaction (6). The rate constant is $k_6 = 0.9 \times 10^6$ M^{-1} s^{-1} for $HO_2{}^{\bullet}$ which has p$K_a = 4.8$, whereas $k_6 < 0.3$ M^{-1} s^{-1}, for $O_2{}^{\bullet -}$ in the alkaline range [12]. Reaction (7a) does not take place for ketone [15].



Scheme 4.



Scheme 5.

3.4. *Photoreactions of (di)pyridylketones with oxygen and ascorbic acid*

Curves of the O_2 concentration versus irradiation time in the presence of ascorbic acid are linearly decreasing. The quantum yield for irradiation at 313 nm of the pyridylketone/ascorbate system is up to $\Phi_{-O_2} = 0.7$ for irradiation at 313 or 366 nm of 3,3′-Dy. The Φ_{-O_2} values as a function of log of the ascorbic acid concentration show a sigmoidal shape (Fig. 7), indicating that oxygen is consumed, when competition kinetics favour radical formation. Ascorbic acid (AscH) has p$K_a = 4.2$ [42] and the ascorbate radical ($Asc(-H)^{\bullet -}$) terminates via reaction (8) into Asc(–H) (deoxyascorbate, Scheme 5) and Asc^- with a strong pH dependence, at pH 7: $k_8 = 2 \times 10^6$ M^{-1} s^{-1} [13]. The photoinduced reactions of ketones in aqueous solution with ascorbic acid are initiated by electron transfer, reaction (3b), yielding the ketyl radical which reacts with oxygen via reaction (4). The rate constant for the pyridylketones in water at pH 7 is $k_3 = 2 \times 10^9$ M^{-1} s^{-1}, corresponding to $[\text{ascorbic acid}]_{1/2} = 0.1$ mM (Tables 1 and 4). In contrast to the case of formate, the ascorbate radical is not quenched by oxygen, reaction

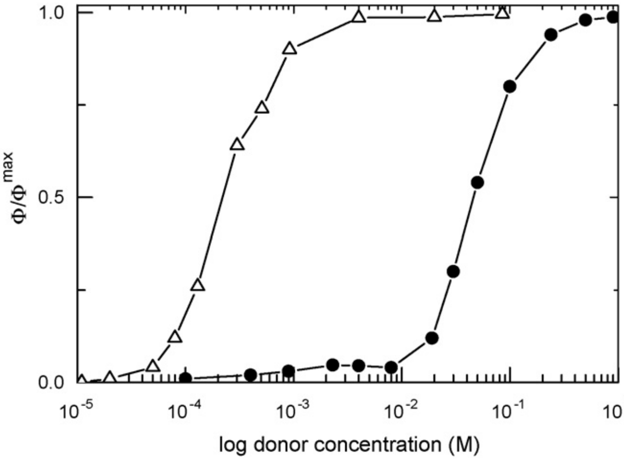


Fig. 7. Semilogarithmic plots of the quantum yield Φ_{-O_2} ($\lambda_{irr} = 313$ nm) as a function of the ascorbic acid (Δ, pH 2–4) and 2-propanol (●, pH 7) concentrations for 3-By in air-saturated aqueous solution.

(5b), but ascorbic acid reacts via reaction (7b) with $HO_2^{\bullet}/O_2^{\bullet-}$ radicals, where $k_7 = 1.2 \times 10^7\ M^{-1}\ s^{-1}$ at pH 2–7 [13].

$$HO_2^{\bullet}/(O_2^{\bullet-} + H^+) + AscH/(Asc^- + H^+) \rightarrow H_2O_2 + Asc(–H)^{\bullet-} + H^+ \quad (7b)$$

$$2 \times Asc(–H)^{\bullet-} \rightarrow Asc^- + Asc(–H) \quad (8)$$

Photodamage occurs in the presence of both ascorbic acid and oxygen. This is mainly caused by formation of hydrogen peroxide via reaction (3b) of the triplet state with ascorbic acid, reaction (4) of the ketyl radical with oxygen and reaction (7b). The photolytical and thermal H_2O_2 formation steps are clearly separated, as shown by the constant O_2 concentration in the time range prior to irradiation or by the nearly constant $[O_2]$ at longer times without illumination. For 3-By and 1 mM ascorbic acid $\Phi_{-O_2} = 0.5$ in both the absence and presence of 10 mM phosphate buffer at pH 3 and 7, respectively.

3.5. Photoreactions of (di)pyridylketones with oxygen and alcohols

Plots of the O_2 concentration versus time using variable intensities are shown in Fig. 8 for 3-By in air-saturated 2-propanol–water. The slope is proportional to the irradiation intensity and the quantum yield is up to 0.5 for 3-By and 3,3′-Dy. Upon irradiation at 280 nm the values are similar and 0.4 for irradiation at 366 nm (Table 3). The Φ_{-O_2} values as a function of log 2-propanol concentration show a sigmoidal shape (Fig. 7). The triplet state is quenched by alcohols via H-atom abstraction leading to the alcohol radical and the ketyl radical. The pK_a of the 2-hydroxy-2-propyl radical is 12.2 [14]. Reaction (3c) under air in the presence of alcohols takes place when the donor concentration is sufficiently high. The ketyl radical is essentially converted back into the ketone, reaction (4). Alcohol radicals are involved in reaction (5c) with oxygen, whereby a peroxyl radical is an intermediate. The rate constant of quenching is $k_5 = (1–9) \times 10^9\ M^{-1}\ s^{-1}$ for the 2-hydroxy-2-propyl radical [15,43].

$$R_2{}^{\bullet}COH + O_2 \rightarrow R_2COHO_2^{\bullet} \quad (5c)$$

$$R_2COHO_2^{\bullet} \rightarrow R_2C{=}O + O_2^{\bullet-} + H^+ \quad (5'c)$$

Eventually, $O_2^{\bullet-}$ is converted into H_2O_2 [14] and 2-propanol is essentially transformed via the 2-hydroxy-2-propyl radical into acetone. Reaction (3c) also successfully competes with reaction (2) in the presence of 1–5 M methanol or ethanol. For Bp and other ketones k_3 is small in the presence of *tert*-butanol and therefore Φ_{-O_2} is very low [15]. Surprisingly, for 3-By and 3,3′-Dy in the presence of 5 M *tert*-butanol the values are much larger, $\Phi_{-O_2} = 0.1$, indicating H-atom transfer to a large extent. Such a reaction is, however, not known for Bp. The $[tert\text{-butanol}]_{1/2} = 1$ M for 3-By can be compared to the much smaller $[2\text{-propanol}]_{1/2}$ value of 0.05 M, reflecting the differences in $1/k_3$. The transient absorption spectra of 3-By (Fig. 2) and 3,3′-Dy in argon-saturated water/2-propanol at pH 7 and 13 show formation of the LAT. Air-saturation leads to fast decay of the ketyl radical.

3.6. Photoreactions of (di)pyridylketones with oxygen and amines

Plots of the O_2 concentration versus irradiation time are shown in Fig. 9 (inset) for 3-By in presence of TEA. The Φ_{-O_2} values as a function of log [TEA] show a sigmoidal shape (Fig. 9). The maximum quantum yield is $\Phi_{-O_2} = 0.5$. The k_3 values, due to quenching via electron transfer, are compiled in Table 1. To keep the DEA, DHA or TEA (Et_2RN, R: H, OH or Et, respectively) in aqueous solution reactive, a pH >10 is necessary [44]. Concerning the pH dependence of Φ_{-O_2} it is worthwhile noting that protonation of the amino group in aliphatic amines causes a strong decrease in reactivity, except for EDTA. Φ_{-O_2} of the 3-By/TEA system is more than 10 times smaller in the presence of 0.03 M phosphate buffer at pH 7–8. EDTA as dis-

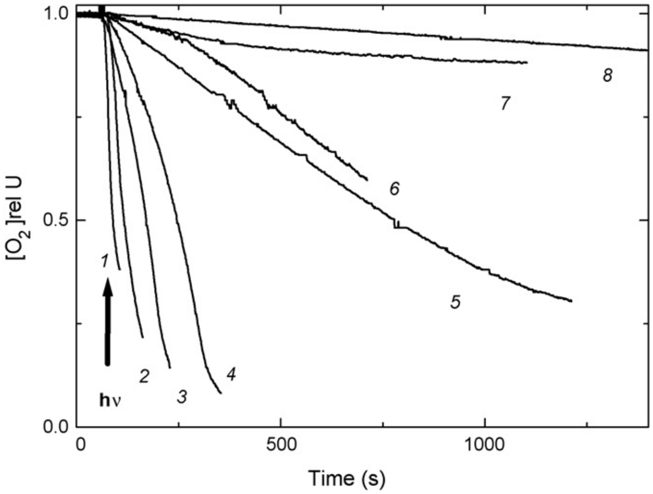


Fig. 8. Plots of the O_2 concentration vs. irradiation time (313 nm) for 3-By in air-saturated aqueous solution at pH 7 in the presence of 0.2 M 2-propanol; the intensity was reduced by a factor of 1, 0.5, 0.24, 0.12, 0.06, 0.03, 0.015 and 0.007: 1–8, respectively.

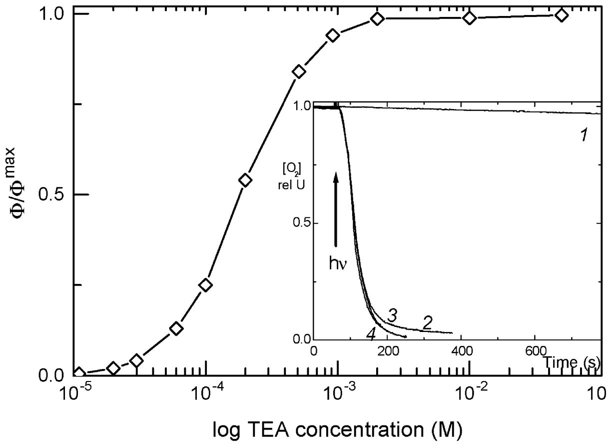


Fig. 9. Semilogarithmic plot of the quantum yield $\Phi_{-O_2^{\bullet}}$ ($\lambda_{irr} = 313$ nm) as a function of the TEA concentration for 3-By in air-saturated aqueous solution; insets: plots of the O_2 concentration vs. irradiation time in the presence of TEA (0.01, 0.2, 2 and 10 mM 1–4, respectively).

odium salt was used for 3-By in aqueous solution at pH 6–8: $k_3 = 2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ and $\Phi_{-\mathrm{O_2}} = 0.4$ (Tables 1 and 3).

The radical cation $\mathrm{Et_3N^{\bullet+}}$ forms the α-aminoethyl radical (Scheme 5) due to deprotonation reaction (9) and/or an equilibrium with the amine yielding $\mathrm{Et_2RNH^+}$ and $\mathrm{EtRN{-}^{\bullet}CHMe}$ [44,45].

$$\mathrm{Et_2RN^{\bullet+}} \rightarrow \mathrm{EtRN{-}^{\bullet}CHMe} + \mathrm{H^+} \qquad (9)$$

$$\mathrm{EtRN{-}^{\bullet}CHMe} + \mathrm{Ar_2C{=}O} + \mathrm{OH^-} \rightarrow \mathrm{EtRNCH{=}CH_2} + \mathrm{Ar_2CO^{\bullet-}} + \mathrm{H_2O} \qquad (10)$$

$$\mathrm{EtRN{-}^{\bullet}CHMe} + \mathrm{O_2} \rightarrow \mathrm{EtRNCH{=}CH_2} + \mathrm{O_2}^{\bullet-} + \mathrm{H^+} \qquad (5d)$$

Reaction (10) of the $\mathrm{Et_3N{-}^{\bullet}CHMe}$ radical occurs with a rate constant of $k_{10} = (0.5\text{–}1) \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$ for phenylnaphthalimines [39] and ketones [15]. Under air, however, reaction (5d) is more efficient than reaction (10). For trimethylamine, where $k_5 = 3.5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$, hydrogen peroxide is a photoproduct [45]. The photolytical and thermal $\mathrm{H_2O_2}$ formation steps are clearly separated, as shown by the different slopes in the time ranges prior to and during irradiation (Fig. 9, inset).

$\Phi_{-\mathrm{O_2}} = 2.9$ and 4.2 have been reported by Bartholomew and Davidson [26] for the photosensitized oxidation of Bp in benzene using 0.1 and 0.3 M TEA, respectively. This indicates a special chain reaction in a medium of low polarity, which is TEA concentration dependent and does not take place for DEA under the same conditions. Virtually the same $\Phi_{-\mathrm{O_2}}$ value below 1 was found for Bp in aqueous solution and both amines [15]. This is comparable to the results for the 3-pyridylketone/amine system (Table 3). The transient absorption spectra of 3-By in argon-saturated water at pH 7 and 13 in presence of TEA (Fig. 3a and b) show formation of the LAT. Air-saturation leads to fast decay of the ketyl radical and a small $\Phi_{-\mathrm{py}}$ for both 3-By and 3,3′-Dy (Table 2). A different case results for 1,4-diazabicyclo[2.2.2]octane, where the rate constant is ca. $1 \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$, but $\Phi_{-\mathrm{O_2}}$ (not shown) is very low. The main reason is efficient electron back transfer from $\mathrm{Ar_2CO^{\bullet-}}$ (under argon) or $\mathrm{O_2}^{\bullet-}$ (in the presence of oxygen) to the radical cation: $\mathrm{DABCO^{\bullet+}}$.

3.7. *Photoprocesses of methylphthalimide*

Examples of the $\mathrm{O_2}$ concentration versus time are shown in Fig. 10 for Me-Pi. The $\Phi_{-\mathrm{O_2}}$ values for Me-Pi in the presence of the donors are markedly smaller than for the two ketones (Table 3). This does not reveal that the mechanism is different, but that the contribution of physical quenching in competition to steps (3a)–(3d) is much larger. The reactivity is also smaller with respect to the two pyridylketones (Table 1), but comparable to the values of Bp and a few other ketones [15]. For example, $k_3 = 1 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ for Me-Pi/DHA. Moreover, no conversion could be registered for formate and 2-propanol at concentrations up to 1 and 7 M, respectively. Taking $\tau_T = 0.5\ \mu\mathrm{s}$ it follows that the half-concentration $[\mathrm{DHA}]_{1/2}$ is 2 mM. This is similar for EDTA and ascorbic acid (Table 4). A half-concentration is a measure for the photooxidative power on the donor.

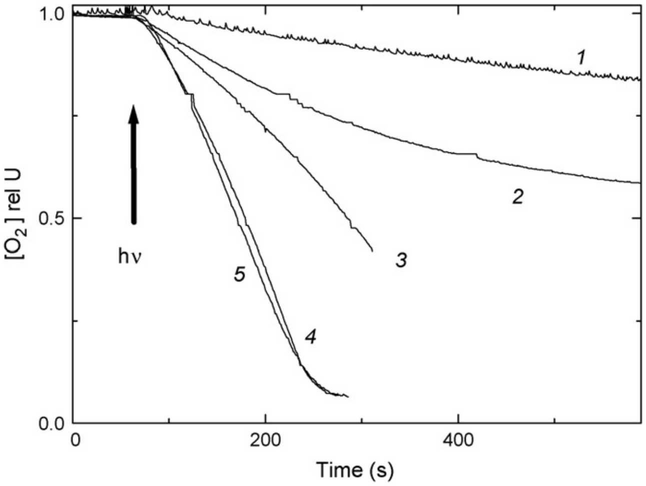


Fig. 10. Plots of the $\mathrm{O_2}$ concentration vs. irradiation time (313 nm) for Me-Pi in air-saturated aqueous solution in the presence of formate (0.1 and 1 M), 1 M 2-propanol, 10 mM TEA and 10 mM ascorbic acid, 1–5, respectively).

3.8. *Photoreactivity in the presence of oxygen*

The reactivity of triplet ketone or phthalimide with each of the four donor types is large for ascorbic acid and amines, smaller for formate or 2-propanol and smallest for *tert*-butanol (Table 1). This is mainly due to the changes in the redox potentials of ketone and donor and the triplet energy level [15]. The same holds for the increase in k_3 on going from alcohols or formate to ascorbic acid or aliphatic amines. Where the mechanism is H-atom transfer, i.e. alcohols or formate, a charge transfer contribution is probably involved. The *tert*-butanol case for the two pyridylketones is remarkable because $\Phi_{-\mathrm{O_2}}$ is very small for Bp (not shown). These $[\mathrm{donor}]_{1/2}$ values can be compared with those obtained from the $1/(\tau_T \times k_q)$ were τ_T refers to air-saturated conditions. The agreement between both, calculated and measured concentration dependences of $\Phi_{-\mathrm{O_2}}$ is reasonable (Table 4).

A $\Phi_{-\mathrm{O_2}}$ value of 2 could be possible, when Φ_{isc} is unity and each oxygen radical is converted into $\mathrm{H_2O_2}$. The maximum quantum yield is close to unity for the formate, 2-propanol, ascorbic acid or amine cases. For the sake of simplicity we assume that Φ_{isc} is unity throughout. In the ascorbic acid case, where reaction (5b) is not operative, one could assume that $\Phi_{-\mathrm{O_2}}$ is up to 1 as each superoxide radical is transferred into hydrogen peroxide, reaction (8b). In the 2-propanol case, where $\Phi_{-\mathrm{O_2}}$ is up to 0.5, both radicals are formed per photon, i.e. termination step of $\mathrm{Me_2COHO_2}^{\bullet}$ and $\mathrm{HO_2}^{\bullet}/\mathrm{O_2}^{\bullet-}$ is effective. In the amine case both radicals yield a superoxide radical and $\Phi_{-\mathrm{O_2}}$ is, due to physical quenching, below the maximum of 1. This holds also for formate. In general, one can exclude chain reactions in the ketone/donor systems examined.

4. Conclusion

The photoreactions of a 3-pyridyl and a 3,3′-dipyridyl ketone in water in the presence of formate, ascorbic acid, alcohols or amines can be analyzed by a common mechanism. Triplet quenching by H-atom or electron transfer from the donor yield ketyl radicals, which converts oxygen into the superoxide radical which eventually dismutates into hydrogen peroxide. Competition kinetics of triplet quenching by oxygen not yielding oxygen radicals account for the concentration dependence of the quantum yield of this oxygen uptake. The maximum Φ_{-O_2} values of the ketones examined are 0.4–0.7. The dependences of Φ_{-O_2} as a function of the donor concentration indicate that photodynamic damage of type II does not uptake oxygen in measurable amounts. For *N*-methylphthalimide comparable or lower values were obtained, supporting the same reaction mechanism.

Acknowledgements

The author thanks Professor Wolfgang Lubitz for his support, Dr. Aldo Romani and Professor G. Favaro from Perugia for providing 3,3′-Dy and Mrs. Daniela Hoffmann, Mr. Christian Lemsch, Horst Selbach and Leslie J. Currell for technical assistance.

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