

Photoinduced oxygen uptake for benzoylpyridines and dipyritylketones in aqueous solution

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ABSTRACT

The photochemical properties of 4-benzoylpyridine (4-By) and 4,4'-dipyritylketone (4,4'-Dy) were studied in air-saturated aqueous solution in the presence of formate, ascorbic acid, amines and alcohols as appropriate donors. Upon UV irradiation of these systems oxygen is consumed. The quantum yield of oxygen uptake increases with the donor concentration, approaching $\Phi_{-O_2} = 0.2-0.8$, e.g. for 4-By and 4,4'-Dy in the presence of ascorbic acid or triethylamine (0.3–30 mM), 0.03–1 M formate and 0.1–10 M 2-propanol. Quenching of the triplet state by the donor and subsequent reaction of both acceptor and donor radicals with oxygen was found. The operating mechanism is oxidation of the donor and conversion of oxygen via the hydroperoxyl radical into hydrogen peroxide. The relevant properties of donors, the radicals involved and the concentration dependencies are discussed. For 2-By and 2,2'-Dy oxygen is also converted into H_2O_2 . The mechanism of the 2-pyridyl isomers in the presence of oxygen, however, differs from that of the $n=3,4$ isomers in the respect that the photoreaction is due to ring closure and dehydrogenation. The photoinduced oxygen-uptake with 2-By and 2,2'-Dy therefore takes place in the absence of a donor and $\Phi_{-O_2} = 0.3-0.4$.

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1. Introduction

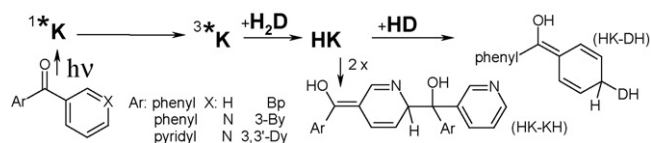
The photophysical and photochemical properties of n -benzoylpyridines (Bys) and n,n' -dipyritylketones (Dys), $n=2-4$, which are heterocyclic homologues of benzophenone (Bp), are the subjects of several investigations [1–16]. The position of the nitrogen is a major factor in the photochemistry since cyclization takes place for 2-By and 2,2'-Dy [2,8,12]. The photoreactions for the cases $n=3,4$ are intermolecular electron or H-atom transfer from additives to the ketone triplet state whereby radical intermediates are formed. Recently, identification of the photoproducts of 4-By in 2-propanol has been presented, using a time-resolved resonance Raman technique [16]. Upon photolysis of Bp in the presence of 2-propanol a so-called light absorbing transient (LAT) has been observed [17–19]. LATs are quasi-stable intermediates resulting from radical termination. A structural characterization of the LAT of Bp in 2-propanol, based on time-resolved resonance Raman spectroscopy, has been reported [19]. LATs are also known for 4-By [16] and the 4,4'-Dy/2-propanol system [1]. Their results in deoxygenated aqueous alcohol or amine solution were reported for n -By and n,n' -Dy, $n=3,4$ [3,14,15]. The mechanisms of self-coupling for 3-By and 3,3'-Dy and cross-coupling for Bp and the structures involved are illustrated in Scheme 1.

LAT mechanisms have also been studied for a few heterocyclic systems [20,21]. LAT formation has been discussed for cross-coupling of 2-benzoylthiophene radicals with phenol radicals [21]. The photochemistry of aromatic mono- and diketones is sensitive to oxygen. The photoinduced O_2 uptake/consumption has been studied for 3-By and 3,3'-Dy [14] in air-saturated aqueous solution in the presence of appropriate donors. Photoinduced O_2 uptake has also been studied for ketones and various other systems, e.g. 1,4-naphthoquinone, 9,10-anthraquinone, flavins and xanthene dyes [22]. Four types of donor were chosen: formate, ascorbic acid (vitamin C) as unique radical scavenger, 2-propanol as example of a reactive alcohol and aliphatic amines.

The photodynamic action of a sensitizer generally refers to electron transfer (Type I) yielding hydroperoxyl/superoxide ion radicals ($HO_2^*/O_2^{\bullet-}$) and to energy transfer (Type II) yielding singlet molecular oxygen: $O_2(^1\Delta_g)$ [23–29]. Compilations of the latter quantum yields (Φ_Δ) from biologically relevant molecules are available [25,26]. In addition, the superoxide radical ($HO_2^*/O_2^{\bullet-}$) can be generated, the quantum yield is often small [27]. The kinetic features of the $HO_2^*/O_2^{\bullet-}$ radical in aqueous solution are known from radiolysis [28]. It is interesting to question the role and subsequent fate of oxygen in the photochemistry of other specific heteroaromatic ketones.

In this work the quantum yields of oxygen uptake (Φ_{-O_2}) are presented for 4-By and 4,4'-Dy in air-saturated aqueous solution. UV irradiation leads to the conversion of O_2 into hydrogen peroxide. Φ_{-O_2} is strongly enhanced on addition of H-atom

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Scheme 1.

donors, such as 2-propanol or formate. Likewise, ascorbic acid and several amines, e.g. triethylamine (TEA), diethylamine (DEA), *N,N*-diethylhydroxylamine (DHA) or ethylenediaminetetraacetate (EDTA), enhance Φ_{-O_2} because they act as electron donors. Oxygen quenches the triplet state and scavenges the radicals derived from both the donors and the ketones. The results from quenching of the triplet state by these electron or H-atom donating additives using time-resolved UV-vis spectroscopy at 308 nm are in agreement. For comparison and complementation, 2-By and 2,2'-Dy were also studied in air-saturated aqueous solution without donors.

2. Experimental details

2,2'-Dy and 4,4'-Dy were prepared by Dr. Romani and received as a gift from Professor Favaro. The other compounds (EGA, Sigma) and the solvents (Merck) were commercially available and used as received after checking for impurities; TEA was purified by distillation. Water was from a millipore milliQ system. The UV-vis absorption spectra were monitored on a diode array spectrophotometer (HP, 8453). The molar absorption coefficient of 2-By in water at 260 nm is $\epsilon_{260} = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. For photoconversion the 280 or 313 nm lines of a 1000 W Hg-Xe lamp and a monochromator were used [14,15]. The IR spectra were recorded on a FTIR spectrometer (Bruker IFS66). The pathlength was generally 1.0 cm for UV-vis; the much higher sample concentrations necessary for IR were adjusted to $A_{\text{exc}} = 0.1\text{--}2$ in 0.5 mm CaCl cells. 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. 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 results refer to $\lambda_{\text{exc}} = 308 \text{ nm}$ throughout and pulse intensities of 2–8 MW cm^{-2} , corresponding to an energy of 2–8 mJ. The absorption signals were measured with a digitizer (Tektronix 7912AD) and an Archimedes 440 computer for data handling. The oxygen concentration was determined by a Clark cell (Hansatech) [14] and 0.27 mM was taken as oxygen concentration under air. Alternatively, a fiber optic sensor (Foxy, Ocean Optics) combined with a 470 nm light emitting diode and a fluorimeter (USB 4000) were used. This utilizes the quenching of the luminescence of a ruthenium complex by oxygen. Note that detection is possible during illumination of the samples as long as no significant emission contributed to the detection signal around 600 nm; otherwise detection was determined at time intervals without irradiation. The measurements were carried out under conditions of reduced environmental light. In neutral aqueous solution both methods are comparable, but only the electrochemical cell was used with TEA due to the corresponding high pH. The oxygen concentration generally decreases upon photolysis in a specific way, mostly with a well-defined linear portion. The relative yield of oxygen consumption was determined from the slope vs. irradiation time [14]. The ion concentration was kept low, e.g. pH was

Table 1
Rate constants for quenching ($10^9 \text{ M}^{-1} \text{ s}^{-1}$) by donors^a.

	4-By	4,4'-Dy	3-By	3,3'-Dy
Formate	0.1	0.3	0.2	0.1
Ascorbic acid	1	1	2	2
2-Propanol	0.06	0.1, 0.05 ^b	0.04	0.02
TEA	1 ^c	5	2	2
EDTA	2	3	2	2

^a In argon-saturated aqueous solution, $\lambda_{\text{exc}} = 313 \text{ nm}$, typical donor concentrations are 1 mM for amines and ascorbic acid, 0.03 M for formate and 0.2 M for alcohols; values for 3-By and 3,3'-Dy were taken from Ref. [14].

^b Using ethanol.

^c Similar value for DEA.

close to 7 in the presence of alcohols or formate. 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 [14]. All heteroketones refer to trans isomers and the measurements were carried out at 24 °C.

3. Results

3.1. Triplet properties of 4-By and 4,4'-Dy

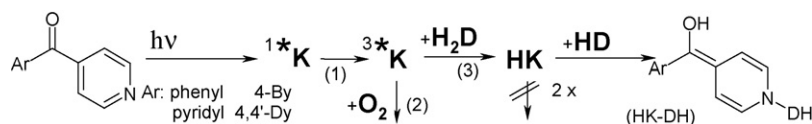
The mechanism of LAT formation is illustrated in Scheme 2. The triplet is populated via reaction (1), quenching by oxygen (2) competes with quenching by the respective donor, reaction (3). The T-T absorption spectra of 4-By and 4,4'-Dy in aqueous solution have a major maximum at 320 nm and a minor one at 520 nm [15] and are reminiscent to that of Bp. The triplet lifetimes of 4-By and 4,4'-Dy in air-saturated aqueous solution at pH 6–8 are $\tau_T = 1.9$ and 3.1 μs , respectively. The respective rate constants for quenching of the triplet state by oxygen are $k_2 = 2.1 \times 10^9$ and $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Quenching reaction (2) of triplet ketones is expected to yield singlet molecular oxygen [25,26]. The rate constant k_3 was determined from plots of $1/\tau_T$ vs. the donor concentration and ranges from 6×10^7 to $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1).

3.2. Spectral changes of 4-By and 4,4'-Dy in the UV and IR

Examples of the absorption spectra of 4-By and 4,4'-Dy in air-saturated solution in the ultraviolet and infrared ranges are shown in Figs. 1 and 2, respectively. The absorption band at 280 nm of 4-By in 2-propanol decreases upon irradiation by UV light (Fig. 1a) and a secondary photoprocess with a band centered at 434 nm is indicated by curve 4. The UV-induced spectra of 4,4'-Dy show a conversion into the nearly colorless product, but isosbestic points at 240, 270 and 310 nm (Fig. 2a). The IR absorption spectra of 4,4'-Dy in acetonitrile mixed with 1 vol% 2-propanol show two bands at 1630 and 1680 cm^{-1} , a corresponding conversion with a product peak at 1713 cm^{-1} and an isosbestic point at 1690 cm^{-1} (Fig. 2b). An isosbestic point at 1690 cm^{-1} and similar but less significant spectra were recorded for 4-By (Fig. 1b).

3.3. Photoinduced oxygen uptake with 4-By and 4,4'-Dy

Upon UV irradiation at 280 or 313 nm of heteroketones 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 $[O_2]$ signal vs. time are shown in Fig. 3 for 4,4'-Dy. The plots of



Scheme 2.

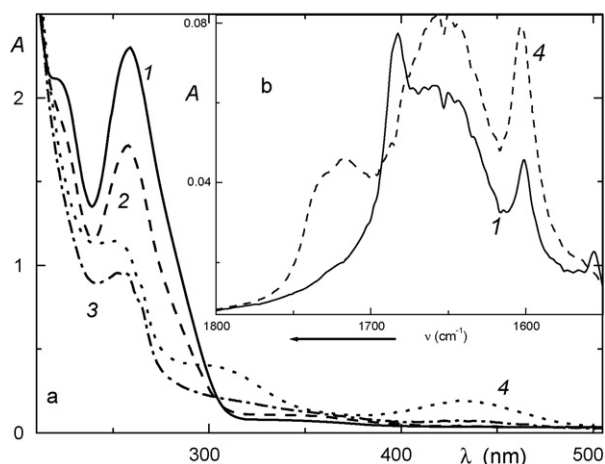


Fig. 1. (a) UV/vis and (b) IR absorption spectra of 4-By in air-saturated 2-propanol prior to (1) and after 0.5, 1 and 5 min (2–4) irradiation at 280 nm.

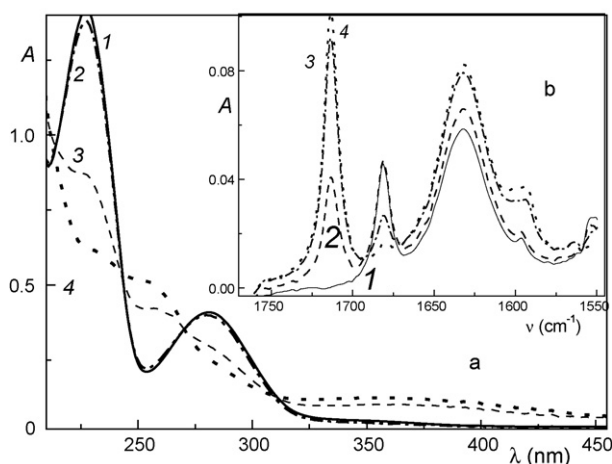


Fig. 2. (a) UV/vis and (b) IR absorption spectra of 4,4'-Dy in air-saturated acetonitrile–2-propanol (99:1) prior to (1) and after 1, 2 and 5 min (2–4) irradiation at 280 nm.

the oxygen concentration vs. irradiation time in presence of donors are downward curved, reach a major linear part and level off. The slope of this linear part is proportional to the irradiation time or intensity and taken to be a relative quantum yield of the O_2 con-

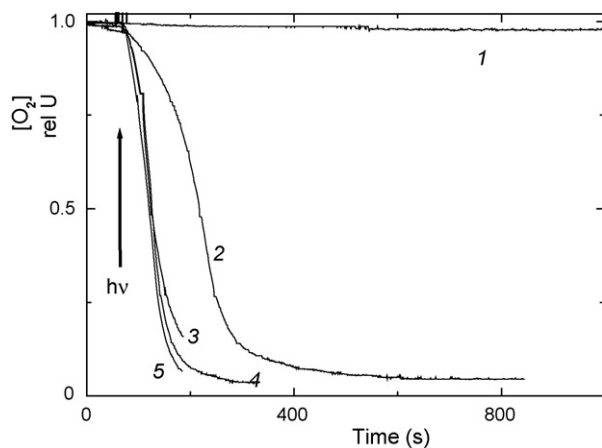


Fig. 3. Plots of the oxygen concentration as a function of the irradiation time for 4,4'-Dy in air-saturated aqueous solution (1) and in the presence of methanol (0.1 M, 2), formate (0.1 M, 3), TEA (1 mM, 4) and ascorbic acid (1 mM, 5), $\lambda_{\text{irr}} = 313$ nm.

Table 2
Quantum yield of oxygen uptake (Φ_{-O_2}) in the presence of donors^a.

	4-By ^b	4,4'-Dy ^b	3-By	3,3'-Dy
Formate	0.7	0.6	0.6	0.6
Ascorbic acid	0.4	0.6	0.5	0.7
2-Propanol	0.6	0.6	0.5	0.5
TEA	0.6 ^c	0.5	0.4	0.5
DHA	0.5	0.4	0.4	0.3
EDTA	0.5	0.6	0.3	0.4

^a In air-saturated aqueous solution, donor concentrations as in Table 1, $\lambda_{\text{irr}} = 313$ nm; values for 3-By and 3,3'-Dy were taken from Ref. [14].

^b In the absence of a donor $\Phi_{-O_2} < 0.01$.

^c Similar value for DEA.

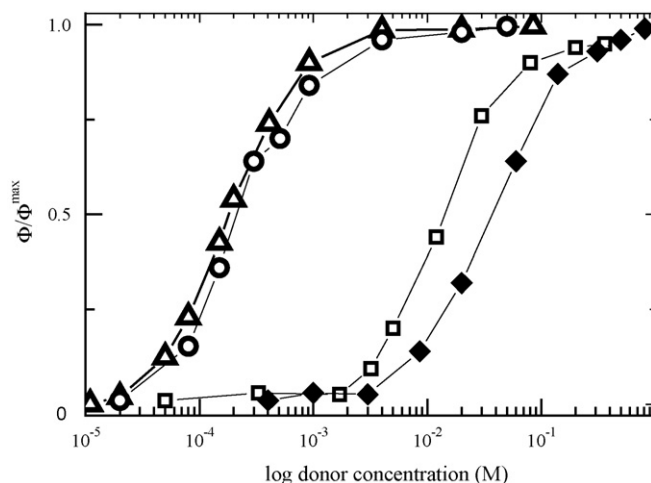


Fig. 4. Semilogarithmic plots of Φ_{-O_2} as a function of the ascorbic acid (circles), TEA (triangles), formate (squares) and 2-propanol (diamonds) concentration for 4-By (full) and 4,4'-Dy (open) in air-saturated aqueous solution, $\lambda_{\text{irr}} = 313$ nm.

sumption. In the presence of 1–10 mM ascorbic acid Φ_{-O_2} of 4-By is smaller than of 4,4'-Dy, whereas for several amines and alcohols the differences are minor (Table 2). When no donor is added Φ_{-O_2} is negligibly small. Semilogarithmic plots of Φ_{-O_2} as a function of the donor concentration are sigmoidal, approaching a maximum value. Examples are shown in Fig. 4 for 4-By and 4,4'-Dy.

3.4. Photoinduced oxygen uptake with 2-By and 2,2'-Dy

The absorption spectra of 2,2'-Dy in air-saturated aqueous solution at pH 7–8 upon irradiation at 313 nm exhibit isobestic points at 264 and 277 nm (not shown). The products of 2-By and 2,2'-Dy are hetero-fluorenones and for 2-By the quantum yield of this cyclization has been reported to be $\Phi_{\text{Cy}} = 0.2$ [2]. UV irradiation of 2-By and 2,2'-Dy in air-saturated aqueous solution causes efficient oxygen uptake without any additive. Plots of the O_2 concentration, obtained with the Clark cell as a function of the time of irradiation at 313 nm, are shown in Fig. 5 and examples obtained with the fiber optic sensor are shown in the inset. For 2-By and 2,2'-Dy $\Phi_{-O_2} = 0.3$ and 0.4, respectively. Consumption of oxygen in the photolysis is due to ring closure and dehydrogenation, whereby oxygen is converted into H_2O_2 .

4. Discussion

4.1. Photoreactions of para-(di)pyridylketones with donors

The reactions of the triplet state of (di)pyridylketones with donors are initiated by electron transfer from amines or ascorbic acid; H-atom transfer takes place in the cases of formate,

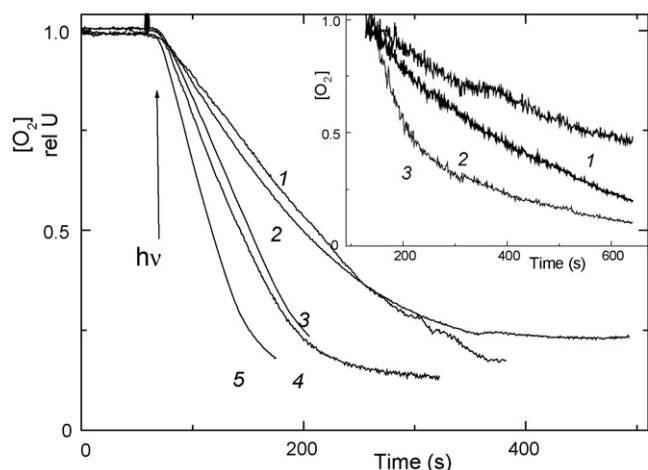


Fig. 5. Plots of the oxygen concentration, obtained with the Clark cell, as a function of irradiation time for 2,2'-Dy in air-saturated aqueous solution (concentrations of 0.01, 0.03, 0.3 and 1 mM: 1–4, respectively) and 2-By (5), $\lambda_{\text{irr}} = 313$ nm; inset: signals obtained with the fiber-sensor for 2-By with UV transmission of 12, 25 and 100%, 1–3, respectively.

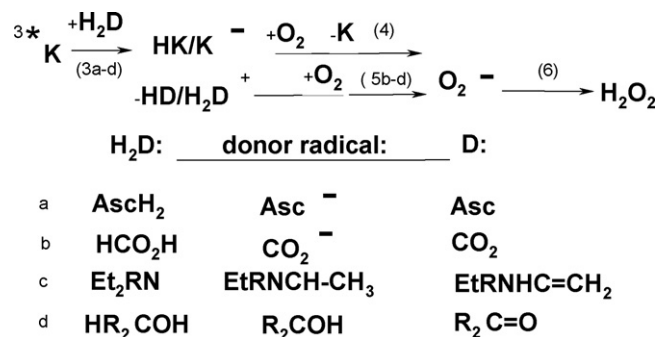
2-propanol or other alcohols [1,15]. The quantum yields of decomposition (Φ_{py} , $\lambda_{\text{irr}} = 254$ nm) of 4-By and 4,4'-Dy in the presence of donors and absence of oxygen are $\Phi_{\text{py}} = 0.3$ –0.7 using concentrations of 0.001, 0.003, 0.1 and 0.3 M, for ascorbic acid, amines, formate and alcohols, respectively [15]. The radicals of the donor and 4-By react into LATs with a maximum at about 370 nm which disproportionate in the ms-s time scale forming phenyl-4-pyridylmethanol as a stable species. The LATs of 4,4'-Dy absorb up to 500 nm, have similar decay rate constants and eventually form 4-dipyridylmethanol. Formate, alcohols or amines are favorable to induce LATs, in contrast to ascorbic acid. The disproportionation kinetics shown in Scheme 2 support a cross-coupling reaction mechanism for formation of LATs [15].

4.2. Photoreactions of para-(di)pyridylketones with oxygen and ascorbic acid

Ascorbic acid is known to enhance the quantum yield Φ_{O_2} as a measure of the conversion of oxygen via the superoxide radical into hydrogen peroxide [14]. The curve of the O_2 concentration vs. irradiation time in the presence of ascorbic acid decreases linearly (Fig. 3). The quantum yield for irradiation at 313 nm of the pyridylketone/ascorbate system is up to $\Phi_{\text{O}_2} = 0.2$ –0.6 (Table 2). The Φ_{O_2} values as a function of the log of the ascorbic acid concentration show a sigmoidal shape (Fig. 4), indicating that oxygen is consumed, when competition kinetics favor radical formation. Photodamage occurs in the presence of both ascorbic acid and oxygen. This is mainly caused by formation of hydrogen peroxide via reaction (3a) of the triplet state with ascorbic acid, reaction (4) of the ketyl radical with oxygen, Scheme 3. $\text{O}_2^{\bullet-}$ is converted in H_2O_2 via step (6). The rate constant is $k_6 = 0.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for HO_2^{\bullet} which has $\text{p}K_{\text{a}} = 4.8$, whereas $k_6 < 0.3 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{O}_2^{\bullet-}$ in the alkaline range [28,29]:



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 $[\text{O}_2]$ at longer times without illumination. Ascorbic acid ($\text{AscH}_2/\text{AscH}^-$) has $\text{p}K_{\text{a}} = 4.1$. The photoinduced reactions of the pyridylketones in aqueous solution with ascorbic acid are initiated by electron trans-



Scheme 3.

fer, reaction (3a), yielding the ketyl radical anion which reacts with oxygen via reaction (4). The rate constant for the pyridylketones in water at pH 3–4 is $k_3 = (1\text{--}2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1). This corresponds to a half-concentration, $[\text{ascorbic acid}]_{1/2} = (0.1\text{--}0.2) \text{ mM}$ (Table 3), i.e. the donor concentrations for 50% of the maximum Φ_{O_2} values. The ascorbate radical ($\text{Asc}^{\bullet-}$) terminates via reaction (7) into deoxyascorbate: $k_7 = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7 [29]. In contrast to other donors, the ascorbate radical is not quenched by oxygen, but ascorbic acid reacts via reaction (8) with $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$ radicals, where $k_8 = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 2–7 [28,29]. The acceptor radical under argon has half-lives of 0.2–2 ms under our conditions, whereas air-saturation leads to fast decay typically in the μs range (not shown):



4.3. Photoreactions of para-(di)pyridylketones with oxygen and formate

The Φ_{O_2} values increase with the formate concentration (Fig. 4) and Φ_{O_2} is 0.3–0.6 for irradiation of 4-By and 4,4'-Dy at 313 nm using 0.1–1 M formate (Table 2). The reactions of formate with the ketone triplets are illustrated in Scheme 3. Quenching occurs via H-atom transfer (3b), whereby the acceptor (ketyl) radical is formed which is converted back into the ketone via reaction (4). Oxygen is also converted into the $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$ radical by reaction (5b) and eventually into H_2O_2 [29,30]. The k_3 values are $(1\text{--}3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1) which is similar to 3-By and 3,3'-Dy [14] and larger than for Bp. The half-concentration is $[\text{formate}]_{1/2} = 16 \text{ mM}$ for 4,4'-Dy (Table 3). The reactions of the formate ion with a triplet state of an acceptor have been studied for 4-carboxybenzophenone and benzophenone-4-sulfonate, where $k_5 = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [30]. The lifetime of the ketyl radical under air was found to be not longer than τ_{T} , i.e. $k_4 > 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Table 3

Experimental values of half-concentration (mM) for Φ_{O_2} in the presence of donors^a.

	4-By	4,4'-Dy	3-By ^b
$[\text{Formate}]_{1/2}$	20	10	6
$[\text{Ascorbic acid}]_{1/2}$	0.1	0.2	0.4
$[\text{2-Propanol}]_{1/2}$	40	50	60
$[\text{TEA}]_{1/2}$	0.1 ^c	0.2	0.3
$[\text{DHA}]_{1/2}$	0.1	0.2	0.5
$[\text{EDTA}]_{1/2}$		0.2	0.5

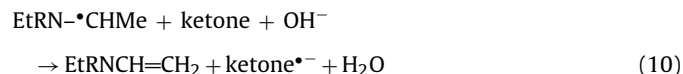
^a In air-saturated aqueous solution, $\lambda_{\text{irr}} = 313$ nm.

^b Taken from Ref. [14].

^c Similar value for DEA.

4.4. Photoreactions of *para*-(di)pyridylketones with oxygen and amines

The maximum quantum yield is $\Phi_{-O_2} = 0.5\text{--}0.7$. The reactions of DEA, DHA or TEA (Et_2RN , R: H, OH or Et, respectively) with triplet ketone are illustrated in Scheme 3. Quenching by amines occurs via electron transfer (3c). To keep the amine in aqueous solution reactive, a quite large pH is necessary [22]. This is not the case for EDTA, whereas the characteristic values, such as k_3 , Φ_{-O_2} and $[\text{amine}]_{1/2}$ are comparable (Tables 1–3). The radical cation $\text{Et}_3\text{N}^{\bullet+}$ forms the α -aminoethyl radical due to deprotonation reaction (9) and reaction (10) of the $\text{Et}_3\text{N}^{\bullet+}\text{CHMe}$ radical with the ketone:



Under air, however, reaction (5c) is more efficient than reaction (10). For trimethylamine, where $k_5 = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, hydrogen peroxide is a photoproduct [29]. The photolytical and thermal H_2O_2 formation steps are clearly separated, as shown for TEA by the constant oxygen concentration in the time range prior to irradiation (Fig. 3).

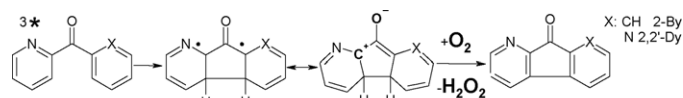
4.5. Photoreactions of (di)pyridylketones with oxygen and alcohols

The triplet state is quenched by alcohols via H-atom abstraction leading to the alcohol radical and the ketyl radical (Scheme 3). Reaction (3d) 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 (5d) with oxygen, whereby a peroxy radical is an intermediate. The rate constant of quenching is $k_5 = (1\text{--}9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the 2-hydroxy-2-propyl radical. Eventually, $\text{O}_2^{\bullet-}$ is converted into H_2O_2 and 2-propanol is essentially transformed via the 2-hydroxy-2-propyl radical into acetone. Reaction (3d) also successfully competes with reaction (2) in the presence of 1–5 M methanol or ethanol. The $[\text{2-propanol}]_{1/2}$ value of 0.05 M reflects the much smaller k_3 with respect to amines. Air-saturation leads to fast decay of the ketyl radical as for the other donors used. For 4,4'-Dy in *tert*-butanol, similar to 3,3'-Dy [15], the ketyl radical and the LAT were recorded. Moreover, for both 4-By and 4,4'-Dy photoreduction takes place even under conditions of air-saturation (Figs. 1 and 2).

With respect to LAT formation the spectral UV–vis changes of 4-By and 4,4'-Dy under air (Figs. 1 and 2a) are much smaller than those in the absence of oxygen [15]. For example, Φ_{-py} of 3-By in the presence of 1 M 2-propanol is 0.9 under argon and 20 times smaller under air [14]. This is an extreme case, taking into account that for Bp [17,18] and generally for heteroketones no LATs are formed, when trace amounts of oxygen are not excluded. Nevertheless, it is remarkable that restoration of the ketone by reaction (4) is not fully possible. On the other hand, the IR changes reveal a similar conversion and gives access to more structural information, which, however would go beyond the scope of this work.

4.6. Photoreactivity of *para*-(di)pyridylketones

The reactivity of triplet ketone with each of the four donor types is large for ascorbic acid and amines, smaller for formate or 2-propanol (Table 1) and smallest for *tert*-butanol. 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.



Scheme 4.

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 Φ_{-O_2} is very small for Bp (not shown). These $[\text{donor}]_{1/2}$ values can be compared with those obtained from the $1/(\tau_T \times k_3)$ where τ_T refers to air-saturated conditions. For 3-By and 3,3'-Dy the agreement between both, calculated and from the concentration dependencies of Φ_{-O_2} is reasonable [15].

The maximum Φ_{-O_2} value 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 (5a) is not operative, one could assume that Φ_{-O_2} is up to 1 as each hydroperoxyl/superoxide radical is transferred into hydrogen peroxide, reaction (8). In the 2-propanol case, where Φ_{-O_2} is up to unity, both radicals are formed per photon, i.e. termination step of $\text{Me}_2\text{COH}_2^{\bullet}$ and $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$ is effective. In the amine case both radicals yield a superoxide radical and Φ_{-O_2} is therefore also up to 1. This holds also for formate. For 4-By and 4,4'-Dy as in the cases of ketones [17,18] and 3-By or 3,3'-Dy [14], a chain reaction can be excluded.

4.7. Mechanism of photoprocess for 2-By and 2,2'-Dy in the presence of oxygen

Irradiation of 2-By and 2,2'-Dy in air-saturated aqueous solution at 313 nm in the absence of a donor causes cyclization and dehydrogenation [2]. The proposed ring closure reactions in the case $n = 2$ is illustrated in Scheme 4 (X: CH or N); only one of several products is shown. Bortolus et al. [8] have suggested for 2-By that a dipolar intermediate is formed which is relatively stable, but converted into the pyrrole ring in the presence of oxygen. The cyclization step in the presence of oxygen is more complex [6] and not presented here.

5. Conclusion

The photoreactions of *n*-pyridyl and *n,n'*-dipyridyl ketones in the presence of a donor are reduction ($n = 3,4$) giving rise to oxygen uptake in air-saturated aqueous solution. The presence of formate, ascorbic acid, alcohols or amines is favorable. 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 Φ_{-O_2} . The maximum values are 0.6–0.9 and the dependencies indicate that photodynamic damage involving singlet molecular oxygen does not contribute to oxygen uptake in measurable amounts.

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