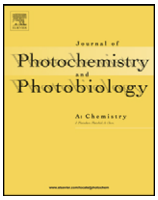
Journal of Photochemistry and Photobiology A: Chemistry 208 (2009) 141–146

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photoinduced oxygen uptake for benzoylpyridines and dipyridylketones in aqueous solution

Helmut Görner

Max-Planck-Institut für Bioanorganische Chemie, D-45413 Mülheim an der Ruhr, Germany

ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 25 August 2009
Accepted 4 September 2009
Available online 15 September 2009

Keywords:
Pyridylketone
Photoreduction
Electron transfer
Light absorbing transient

ABSTRACT

The photochemical properties of 4-benzoylpyridine (4-By) and 4,4′-dipyridylketone (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 $\Phi_{-O_2} = 0.3–0.4$.

1. Introduction

The photophysical and photochemical properties of *n*-benzoylpyridines (Bys) and *n*,*n*′-dipyridylketones (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.

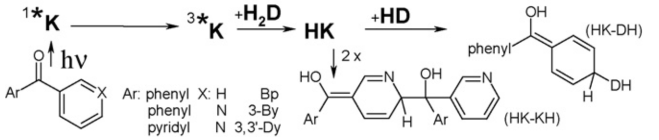
The photodynamic action of a sensitizer generally refers to electron transfer (Type I) yielding hydroperoxyl/superoxide ion radicals ($HO_2^\bullet/O_2^{\bullet-}$) and to energy transfer (Type II) yielding singlet molecular oxygen: $O_2(^1\Delta_g)$ [23–29]. Compilations of the latter quantum yields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

---

E-mail address: goerner@mpi-muelheim.mpg.de.

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.09.007



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 $\varepsilon_{260} = 1.3 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$. 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 $A_{exc} = 0.1–2$ 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 $\lambda_{exc} = 308$ 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 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.

Table 1
Rate constants for quenching ($10^9\ \mathrm{M^{-1}\ s^{-1}}$) 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, $\lambda_{exc} = 313$ 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.

3. Results

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

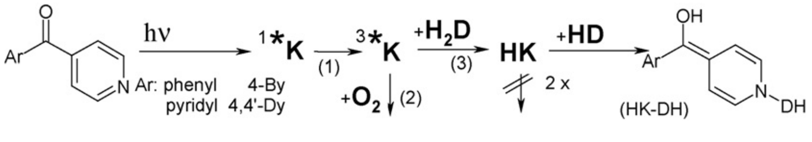
The mechanism of LAT formation is illustrated in Scheme 2. The triplet is populated via reaction (1), quenching by oxygen (2) competes with quenching by the respective donor, reaction (3). The T–T absorption spectra of 4-By and 4,4′-Dy in aqueous solution have a major maximum at 320 nm and a minor one 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 $1.2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. 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 $5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ (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.