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Journal of Photochemistry and Photobiology A: Chemistry 186 (2007) 364–368
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Biphotonic ionization of kynurenine and 3-hydroxykynurenine

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Received 26 July 2006; received in revised form 23 August 2006; accepted 30 August 2006
Available online 23 October 2006

Abstract

The photoionization of kynurenine (KN) and 3-hydroxykynurenine (3OHKN) in aqueous solutions proceeds via a biphotonic mechanism. The precursors for ionization are the triplet states ^{T}KN and ^{T}3OHKN, absorbing the second light quantum. The addition of solvated electrons to the parent molecules with the rate constant 2.0×10^{10} M^{-1} s^{-1} results in the formation of anion radicals, the latter in neutral solutions undergoes fast protonation. The individual spectra of all intermediates – triplet states, cation radicals, electron adducts – formed under UV irradiation of KN and 3OHKN are obtained.

Keywords: Kynurenine; Photoionization; Flash-photolysis

1. Introduction

A group of tryptophan-derived compounds: kynurenine (KN), 3-hydroxykynurenine (3OHKN), 3-hydroxykynurenine glucoside (3OHKG), and 4-(2-amino-3-hydroxyphenyl)-4-oxobutanoic acid glucoside (AHBG), are found in the human lens, where they absorb UV light in the 300–400 nm region protecting the lens and retina from light-induced tissue damage [1–5]. Three of these compounds, KN, 3OHKN and 3OHKG, have been shown to be chemically unstable: at physiological pH and temperature they can undergo deamination or decarboxylation [6,7]. The products so formed, carboxyketoalkenes and aminoketoalkenes, are highly reactive species which can bind to lens proteins [6,8–12]. These reactions can result in the eventual accumulation of the modified proteins in the lens and to the development of a cataract [13,14].

An alternative channel of lens protein modification is the photochemical reactions of the UV filter compounds [15–19]. Kynurenine and most of its derivatives are weak photosensitizers. It has been reported that KN and 3OHKN do not photosensitize the formation of singlet oxygen and superoxide [20], and that the first singlet exited states of these compounds decay to the ground state in picosecond time scale [21], directing light energy into benign channels. Nevertheless, in model experiments the reactions of photoexcited KN with some biological compounds have been observed [22]. In our recent publication [23] we revealed the formation of the KN triplet state under UV irradiation. At physiological pH the quantum yield of the triplet state formation is relatively low, about 2%, and yet this route may be the primary step for the subsequent reactions, resulting in the irreversible chemical modification of the lens proteins.

The present work is aimed at the study of one more potentially harmful photochemical reaction of KN and 3OHKN, photoionization. This reaction is known for aromatic amino acids in aqueous solutions: tryptophan, tyrosine, phenylalanine [24–26]. The intermediates formed – solvated electron and cation radical – can react with other molecules. In particular, the photoionization of tryptophan is one of the major pathways of photo-oxidation of many proteins [27]. The main goals of this work are to demonstrate that photoionization takes place in the photolysis of KN and 3OHKN, to determine the precursor for ionization, and to characterize the short lived intermediates formed under photolysis of these compounds.

2. Experimental details

A detailed description of the LFP equipment has been published earlier [28,29]. Solutions, running through a rectangular cell (inner dimensions 3 mm × 10 mm), were irradiated with a

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doi:10.1016/j.jphotochem.2006.08.026

Quanta-Ray LAB-130-10 Nd:YAG laser (pulse duration 8 ns; 355 nm, pulse energy up to 150 mJ; 266 nm, pulse energy up to 70 mJ). The dimensions of the laser beam at the front of the cell were 2.5 mm × 8 mm. The monitoring system includes a DKSh-150 xenon short-arc lamp connected to a high current pulser, a home-made monochromator, a 9794B photomultiplier (Electron Tubes Ltd.), and a LeCroy 9310A digitizer. The monitoring light, concentrated in a rectangle of 2.5 mm height and 1 mm width, passed through the cell along the front (laser irradiated) window. Thus, in all experiments the excitation optical length was 1 mm, and the monitoring optical length was 8 mm. All solutions were bubbled with argon for 15 min prior to, and during, irradiation.

Actinometry was performed using naphthalene in cyclohexane. The incident laser energy was determined by triplet naphthalene absorption at 414 nm (absorption coefficient $2.45 \times 10^4\ M^{-1}\ cm^{-1}$, triplet quantum yield 0.75 [30,31]).

D,L-Kynurenine and 3-hydroxy-D,L-kynurenine (Sigma/Aldrich) were used as received. Solutions were prepared with the use of phosphate buffers.

3. Results and discussion

Transient absorption spectra, obtained immediately after the 355 nm laser irradiation in the photolysis of Ar-saturated aqueous solutions of KN (2×10^{-4} M) and 3OHKN (2.6×10^{-4} M), are shown in Figs. 1 and 2 by open triangles. A promptly decaying signal on the right-hand side of the spectra was attributed to the solvated electron. Firstly, the spectrum of this intermediate is similar to that of solvated electron; secondly, this signal is readily quenched by well-known electron scavengers, N_2O and acetone. The decay of the signal is monoexponential, the observed decay rate constants k_{obs1} (KN photolysis) and k_{obs2} (3OHKN photolysis) are proportional to the concentration of the initial compounds:

$$k_{obs1} = k_{e1} \times [KN], \quad k_{obs2} = k_{e2} \times [3OHKN]$$

Thus, in our experimental conditions the main channel of solvated electron decay is the attachment to the initial compound. The observed rate constants k_{obs1} and k_{obs2} were measured for the different concentrations of the initial compounds, the calculated rate constants for the electron addition to KN and 3OHKN are $k_{e1} = (2.0 \pm 0.2) \times 10^{10}\ M^{-1}\ s^{-1}$ and $k_{e2} = (1.9 \pm 0.2) \times 10^{10}\ M^{-1}\ s^{-1}$, respectively, which is in a good agreement with the values obtained by pulse radiolysis [32].

The comparison of the spectra, obtained 1 μs after the photolysis of KN in neutral and basic solutions (Fig. 3), shows that in neutral solution the electron adduct $KN^{\bullet -}$ undergoes proto-

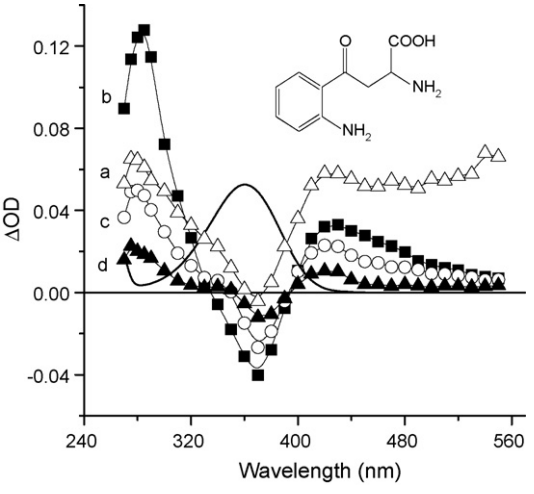

Fig. 1. Transient absorption spectra, obtained in 355 nm photolysis of 2×10^{-4} M KN–(a) open triangles: under Ar, 50 ns after the laser pulse; (b) solid squares: under Ar, 1 μs after the laser pulse; (c) open circles: under Ar in the presence of 5×10^{-3} M acetone, 1 μs after the laser pulse; (d) solid triangles: under O_2 in the presence of 5×10^{-3} M acetone, 1 μs after the laser pulse. Solid line shows the absorption spectrum of KN.

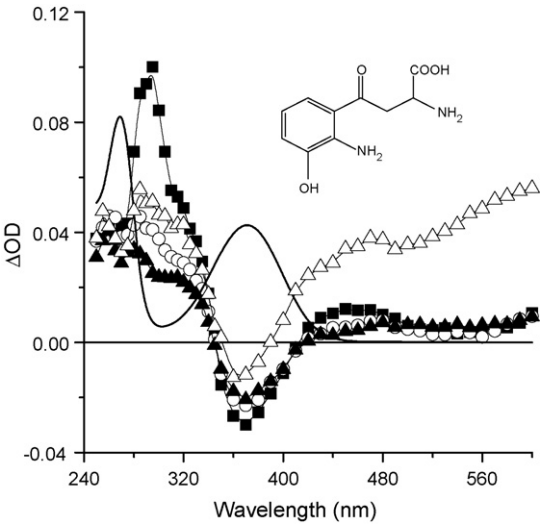

Fig. 2. Transient absorption spectra, obtained in 355 nm photolysis of 2.6×10^{-4} M 3OHKN – open triangles: under Ar, 50 ns after the laser pulse; solid squares: under Ar, 1 μs after the laser pulse; open circles: under Ar in the presence of 5×10^{-3} M acetone, 1 μs after the laser pulse; solid triangles: under O_2 in the presence of 5×10^{-3} M acetone, 1 μs after the laser pulse. Solid line shows the absorption spectrum of 3OHKN.

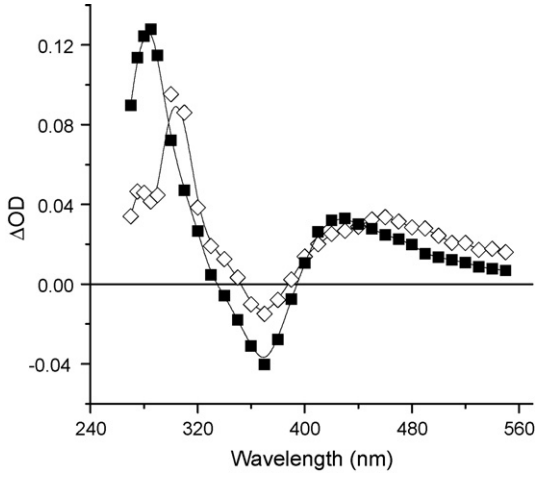

Fig. 3. Transient absorption spectra, obtained 1 μs after 355 nm photolysis of 2×10^{-4} M KN–solid squares: pH 7.0; open diamonds: pH 11.9.