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Wavelength-dependent photochemistry of acetaminophen in aqueous solutions

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ABSTRACT

The influence of irradiation wavelength and intensity on photochemistry of acetaminophen (APAP) in aqueous solution was investigated by combination of steady-state and laser flash photolysis as well as HPLC and LC–MS. Steady-state irradiation at 254 nm leads to APAP disappearance with the quantum yield 0.0014 and to formation of 1-(2-amino-5-hydroxyphenyl)ethanone (**P1**) as a main primary photo-Fries product. In opposite the laser excitation at 266 nm leads predominantly to two-photon ionization of APAP with the quantum yield 0.013 ($I = 70$ mJ/cm^2) and to the formation of one main product of phenoxyl radical reactions – N-(3,4-dihydroxyphenyl)acetamide (**P5**). Steady-state excitation at 282 nm leads to both **P1** and **P5** products formation indicating competition of photo-Fries and photoionization processes. The wavelength-dependent mechanism of APAP photolysis is proposed and discussed.

1. Introduction

In the recent decades, pharmaceuticals and personal care products (PPCPs) in the environment is emerging as a new environmental concern for the scientists and public stakeholders. There are still some residual parts of PPCPs and their metabolites get into the surface and groundwater during and after the sewage treatment [1–6]. In particular, acetaminophen (paracetamol, abbreviated as APAP), a typical kind of PPCPs, which is widely used as an analgesic/antipyretic drug. It was found 58–68% of APAP was excreted from the body during therapeutic use and a median concentration of 0.11 μg l^{-1} was detected in streams [1,7].

The oxidation and degradation of APAP was widely studied by γ-radiolysis [8], UV irradiation in presence of TiO_2 and H_2O_2 [9–12] or (bio)chemical oxidation [13–15]. In all cases the main primary species was APAP phenoxyl radical (RO$^\bullet$) which decays with the formation of coupling, polymeric and hydroxylation products [10,11,13,14]. On the other side, direct UV photolysis of APAP is less studied. In recent papers it was shown that primary product of 254 nm photolysis of APAP is a product of photo-Fries reaction – 1-(2-amino-5-hydroxyphenyl)ethanone (**P1**) [16,17]. This reaction occurs from the singlet excited state of the molecule and involves the migration of the acetyl group onto the aromatic ring in the ortho-position to the amine moiety (reaction 1 [17]). The same mechanism was proposed for other para-substituted acetanilides [18]. This finding was in contradiction with the results of our work in which photoionization with formation of RO$^\bullet$- hydrated electron pair was postulated as a main photochemical process based on data of nanosecond laser flash photolysis at 266 nm [19]. It is indicating that either the light intensity or the irradiation wavelength takes responsibility for the different degradation channels. Actually, although the UV photolysis of various PPCPs have been widely studied, most of the works were investigated under the irradiation at 254 nm and were focused on the effect of aquatic environments (pH, dissolved organic matter, exogenous ions, etc.) on the photo-transformation of the target pollutants. The effects of irradiation

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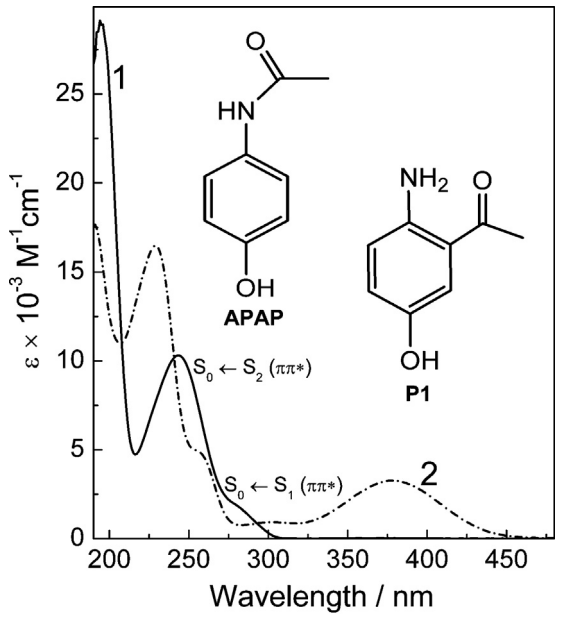
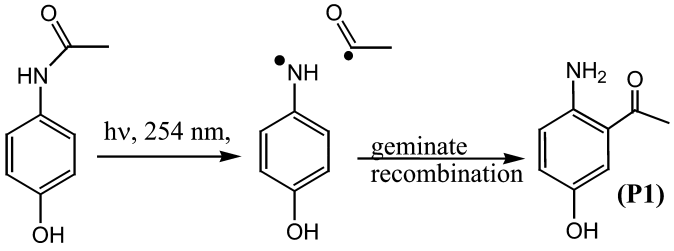


Fig. 1. Structural formulae and absorption spectra of APAP (curve 1) and **P1** (curve 2) in aqueous solution.

conditions on the primary and secondary photochemistry of the investigated compounds were seldom explored.



(1)

So in this work mechanism of direct APAP photolysis was reinvestigated in detail by combination of steady-state (stationary photolysis, HPLC, LC–MS) and time-resolved (laser flash photolysis) methods. The main attention was paid to determination of APAP photolysis quantum yields and product's nature, stability and distribution. It was found that all aforesaid parameters depend on both excitation wavelength and intensity of irradiation.

2. Experimental

2.1. Chemicals

Acetaminophen (98%) was purchased from Alfa Aesar and was used without further purification. 1-(2-Amino-5-hydroxyphenyl)ethanone (**P1**) was synthesized as described in a previous report [20] and have a purity about 97% by HPLC and ^{1}H NMR. Sodium persulfate (chemically pure), $LiClO_4$ (Aldrich), $HClO_4$ (Aldrich) and acetonitrile (HPLC grade) were used without further purification. Absorption spectra and structure of APAP and **P1** are shown in Fig. 1. APAP concentration was in range $(6–50) \times 10^{-5}$ M. The reaction solutions were prepared by doubly distilled water. Unless otherwise specified, all photochemical experiments were performed in a 1 cm quartz cell in air-equilibrated solutions at initial pH 6.5, temperature 298 K and atmospheric pressure.

2.2. Laser flash photolysis

The laser flash photolysis setup based on an LS-2137U Nd:YAG laser (Lotis TII, Belarus) with excitation wavelength of 266 nm, pulse duration of 5–6 ns, illumination spot area of 0.03 cm^2, and energy per pulse up to 10 mJ was used in the time-resolved experiments; the device was similar to that described in previous work [21]. Time resolution of the setup was ca. 50 ns. For steady-state irradiation at 254, 282 and 266 nm Hg low pressure lamp with chlorine and water cut-off filters, XeBr excimer lamp and 4th harmonic of Nd:YAG laser were used, accordingly. Lamps and laser intensity was determined by using ferrioxalate actinomiter in the same conditions as were used for HPLC measurements. The quantum yield of APAP photolysis was calculated from the initial linear decrease of APAP concentration with irradiation time, experiments were done in duplicate, and precision was ca. 20%.

2.3. HPLC analysis

The concentration of APAP in photolyzed solutions was determined by HPLC with UV-detection at 220 nm. HPLC experiments were performed using liquid microcolumn chromatograph Milichrom A-02 with ProntoSIL 120-5-C18 AQ #1810 column, 2.0 mm × 75 mm, 5 μm. The eluent was a mixture of acetonitrile with aqueous buffer solution (0.2 M $LiClO_4$ and 0.005 M $HClO_4$), gradient 5–100% acetonitrile. Flow rate was 100 μl/min, sample volume was 15 μl, and column thermostat temperature was 40 °C.

2.4. LC–MS and LC–MS/MS analysis

LC–MS(/MS) experiments were performed on ESI-q-TOF high-resolution hybrid mass-spectrometer Maxis 4G (Bruker Daltonics, Germany) with the HPLC-separation system UltiMate 3000RS (Dionex, Germany) equipped with ternary pump and diode array UV detection (DAD) in 220–400 nm range. Separation was performed on an analytical column Zorbax XDB-C18, 4.6 mm × 150 mm, 5 μm in the gradient of acetonitrile/0.1% formic acid: 10% (0–2 min), 10–80% (2–20 min), 80–95% (20–21 min), 95% (21–25 min), 95–10% (25–26 min), 10% (26–40 min). Flow rate was 200 μl/min, sample volume was 5 μl, and column thermostat temperature was 40 °C. The instrumental setup allows recording both DAD and MS data simultaneously. Experimental parameters: registration of ions was in the positive mode, range was 50–700 m/z, HV capillary was 4200 V, end plate offset was −500 V, ESI nebulizer pressure was 1.0 bar, dry gas flow (N_2) was 8 l/min, temperature was 200 °C. The instrument was calibrated before each LC–MS(/MS) run with the infusion of the mixture containing sodium formate clusters via switching valve and syringe with the constant flow rate. The acquisition of fragmentation mass spectra (LC–MS/MS) was performed in automatic mode, picking two most abundant ions to be the parent ions for further isolation and fragmentation. After acquiring three good fragment spectra for an ion, the isolated