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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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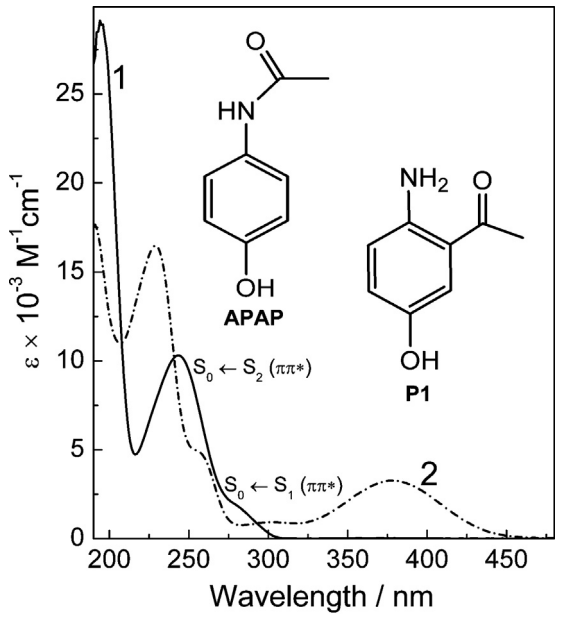
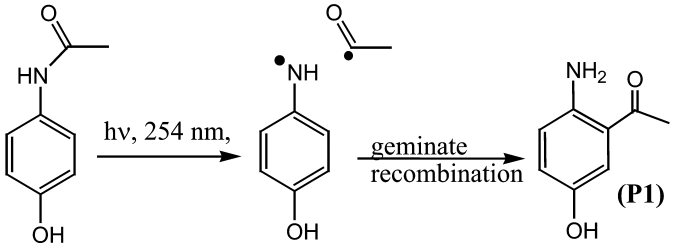


Fig. 1. Structural formulae and absorption spectra of APAP (curve 1) and **P1** (curve 2) in aqueous solution.

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

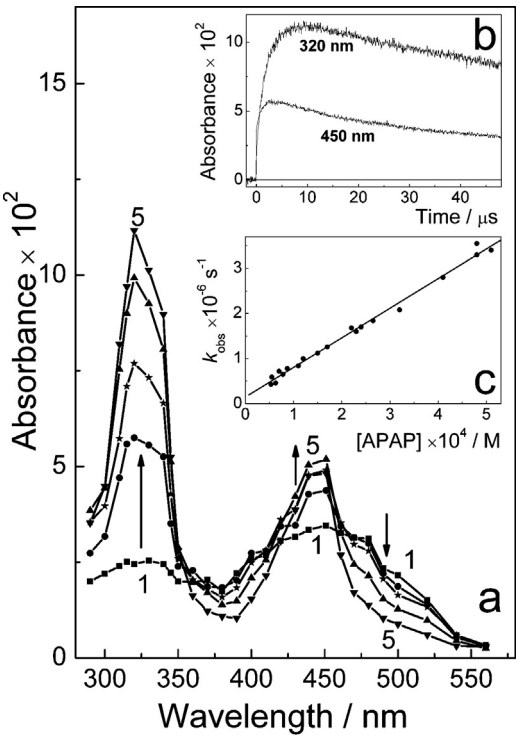


Fig. 2. (a) Transient absorption spectra recorded 0.05 (1), 0.4 (2), 1.6 (3), 4 (4) and 9.6 (5) μs after the laser excitation of $K_2S_2O_8$ (0.04 M) in the presence of APAP (6.5×10^{-5} M). (b) Characteristic kinetic curves at 320 and 450 nm. (c) The dependence of the observed rate constant of RO• radical formation at 320 nm on concentration of APAP.

parent ion was released and the next most abundant ion was picked for the next MS/MS spectra acquisition in LC run.

3. Results and discussion

3.1. Laser flash photolysis of APAP at 266 nm

In our previous paper [19] it was shown that flash excitation of APAP at 266 nm leads to its photoionization with formation of hydrated electron (λ_{max} = 720 nm) – phenoxyl radical (RO•, λ_{max} = 440 nm) pair which is typical behavior for phenols in aqueous solution [22–24]. It was found that RO• decays in self-reaction ($2k/\varepsilon_{440} = 3.3 \times 10^5$ cm × s^{-1}) and reaction with the superoxide radical ($k = 9 \times 10^9$ M^{-1} s^{-1}), which is formed by quenching of the hydrated electron by dissolved oxygen [19].

In order to obtain additional evidence of RO• formation at 266 nm photolysis this species was generated by approach similar to be described in Bispy's work [8]. The oxidation of APAP by photochemically generated one-electron oxidizer $SO_4^{\bullet -}$ radical was done [25].

$$S_2O_8^{2-}(266\,nm) \rightarrow SO_4^{\bullet -} + SO_4^{\bullet -} \quad (2)$$

$$SO_4^{\bullet -} + APAP \rightarrow RO^{\bullet} + SO_4^{2-} \quad (3)$$

The excitation of $K_2S_2O_8$ at 266 nm in presence of APAP leads to the transformation of the initial spectrum of $SO_4^{\bullet -}$ radical (λ_{max} = 455 nm [25]) to the transient spectrum of RO• (Fig. 2a) with maxima at 320 and 445 nm [8]. This spectrum is in agreement with the one obtained in direct photolysis of APAP [19], which proves the formation of RO• upon laser excitation at 266 nm. The rate constant ($k_3 = 6.7 \times 10^9$ M^{-1} s^{-1}) of reaction (3) was calculated from the linear dependence of the observed rate constant of RO• radical formation at 320 nm from the concentration of APAP (Fig. 2c). This

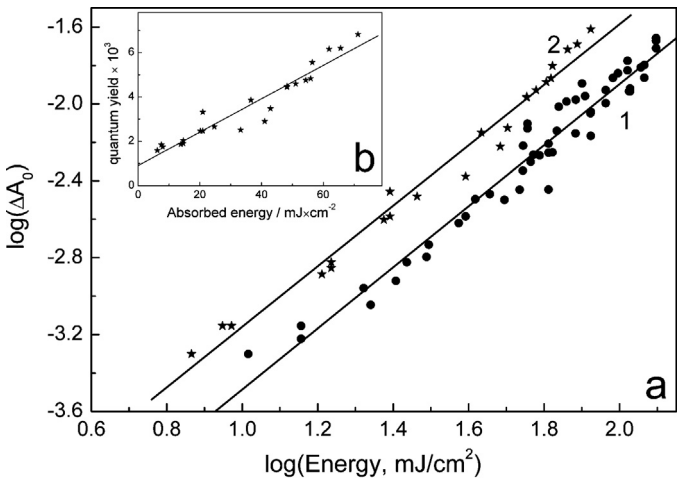


Fig. 3. (a) The dependence of the hydrated electron (λ_{reg} = 720 nm, argon-saturated solutions) and RO• (λ_{reg} = 440 nm, air-equilibrated solutions) yields on laser excitation energy in log–log coordinate. The slope of both lines is 1.6. (b) The dependence of the observed quantum yield of the hydrated electron on excitation energy.

value is close to the diffusion rate constant and to the rate constant of hydroxyl radical reaction with APAP (9.8×10^9 M^{-1} s^{-1} [8]).

In our previous paper practically linear dependence of both hydrated electron and RO• at direct 266 nm photolysis of APAP was observed leading to conclusion that photoionization is monophotonic process mainly [19]. But more accurate measurements in wider range of excitation energy gives slope 1.6 for the yields of species on laser excitation energy in log–log coordinate (Fig. 3). This is clear evidence that two-photon process play the important role in APAP photoionization under laser excitation. The cut-off on the ordinate (Fig. 3, insert) allows to estimate the quantum yield of monophotonic process ($\varphi_{mono} \approx 10^{-3}$).

3.2. Stationary photolysis of APAP and P1

Irradiation at 254 nm leads to APAP disappearance with quantum yield $\varphi^{254} = 1.4 \times 10^{-3}$ and to formation of single main primary product which was identified by optical spectra and LC–MS as photo-Fries product **P1** (retention time 12.5 min, *m*/*z* 152.071, $C_8H_{10}NO_2$, Table 1 and Fig. 4b and c) [16,17]. The formation of one

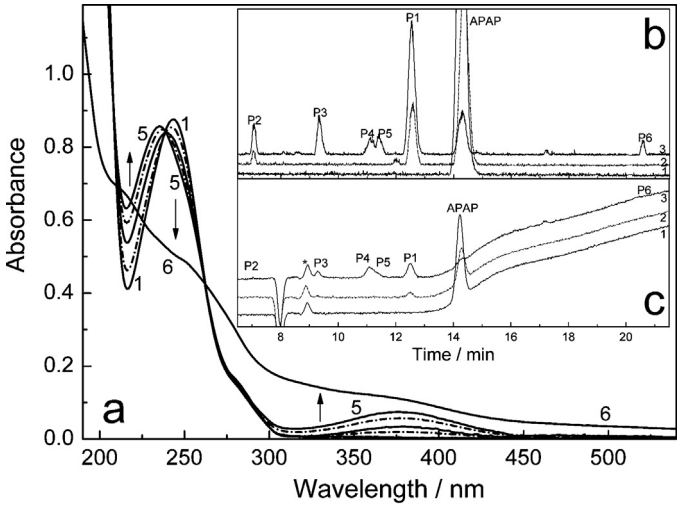
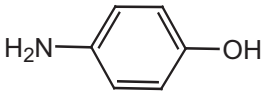
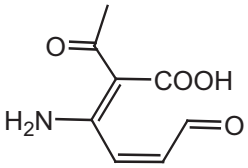
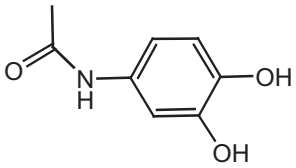
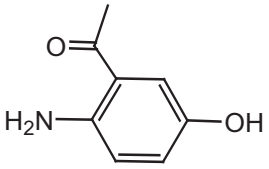
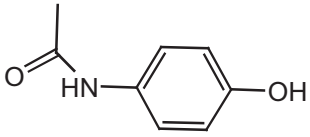
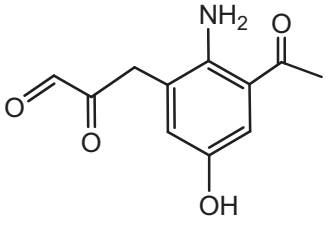


Fig. 4. Optical spectra (a) of air-saturated APAP (8.3×10^{-5} M) solution after 0 (1), 7 (2), 20 (3), 30 (4), 40 (5) and 200 (6) min of irradiation at 254 nm. The base peak (b) and UV (c) chromatograms after 0 (1), 20 (2) and 200 (3) min of irradiation, accordingly. *Impurity in the eluent. The energy of excitation was 6×10^{-4} E × l^{-1} × min^{-1}.

Table 1
LC–MS results of irradiated APAP and **P1**.

RT (min)	Major ESI-MS ions (*m*/*z*)	Structure assignment	Description, compound name and formula
7.1	110.060		**P2**, the minor primary product of APAP photolysis at 254 and 282 nm photolysis 4-aminophenol, C_6H_7NO
9.4	274.070; 256.060; 232.060	–	**P3**, the secondary product of prolonged APAP photolysis at 254 nm $C_{14}H_{12}NO_5$
11.1	184.060; 166.050		**P4**, the secondary product of prolonged APAP photolysis at 254 nm, the main product of photolysis of **P1** at 282 nm (2E,4Z)-2-acetyl-3-amino-6-oxohexa-2,4-dienoic acid, $C_8H_9NO_4$
11.4	168.066; 126.055		**P5**, the main product of 266 nm APAP photolysis and the one of products of APAP photolysis at 282 nm 3-Hydroxyacetaminophen, $C_8H_9NO_3$
12.5	152.071; 134.060; 110.060		**P1**, the main primary product of APAP photolysis at 254 and 282 nm 1-(2-Amino-5-hydroxyphenyl)ethanone, $C_8H_9NO_2$
14.3	152.071; 110.060		Initial APAP Acetaminophen, $C_8H_9NO_2$
20.3	222.076; 204.065; 180.067		**P6**, the minor secondary product of prolonged APAP photolysis at 254 nm 3-(3-Acetyl-2-amino-5-hydroxyphenyl)-2-oxopropanal, $C_{11}H_{12}NO_4$
18.0	287.141	–	**S1**, the main primary product of **P1** photolysis at 282 nm, $C_{16}H_{19}N_2O_3$
21.5	288.124	–	**S2**, the product of prolonged **P1** photolysis at 282 nm, $C_{16}H_{18}NO_4$

photoproduct is also confirmed by conservation of isosbestic points at 239 and 262 nm during initial stages of photolysis (Fig. 4a). The quantum yield of APAP disappearance at 254 nm is rather close to value 10^{-3} published in Martignac's work [17] and is the same order of magnitude as was found for acetanilide (6.6×10^{-3} [26]).

Except **P1** another minor product with retention time 7.1 min was determined as aminophenol (**P2**, *m*/*z* 110.06, $C_6H_{10}NO$, Fig. 4b) in agreement with Martignac's work [17]. Aminophenol is more likely a product of bulk reactions of primary intermediate (aminyl radical) escaped the geminate recombination (reaction (1)).

The prolonged irradiation at 254 nm for 200 min leads to 95% of APAP disappearance and the predominant formation of two secondary products **P5**, (*m*/*z* 168.065, $C_8H_{10}NO_3$) and **P4** (*m*/*z* 184.060, $C_8H_{10}NO_4$) (Fig. 4b, c and Table 1). **P4** is formed most probably due to secondary photolysis of photogenerated **P1**, as **P4** was found to be the product of **P1** photolysis (Fig. 7b). **P4** was also observed as a product of prolonged APAP photolysis in Martignac's work [17]. It was assumed that **P4** is peroxyester R—C(O)—$OOCH_3$ formed by consequence of reactions including the C—C bond photocleavage, the oxygen attachment to CH_3 radical and the recombination of radical species [17]:

$$R{-}C(O){-}CH_3(\mathbf{P1}){-}h\nu \rightarrow R{-}C(O)^{\bullet}\cdots{}^{\bullet}CH_3{-}(O_2) \rightarrow R{-}C(O){-}OOCH_3$$

However, fragment ions of the parent ion (*m*/*z* 184.06) of the **P4** were detected at *m*/*z* 138.053 (loss of HC(O)OH), 124.040 (loss of $CH_2{=}C{=}O$ and H_2O) and 98.057 (loss of $CH_2{=}C{=}O$ and HC(O)OH) (Table 1S and Fig. 2S, ESI). No fragment ions with characteristic mass corresponding to loss of CH_3O, CH_3OO or C(O)—$OOCH_3$

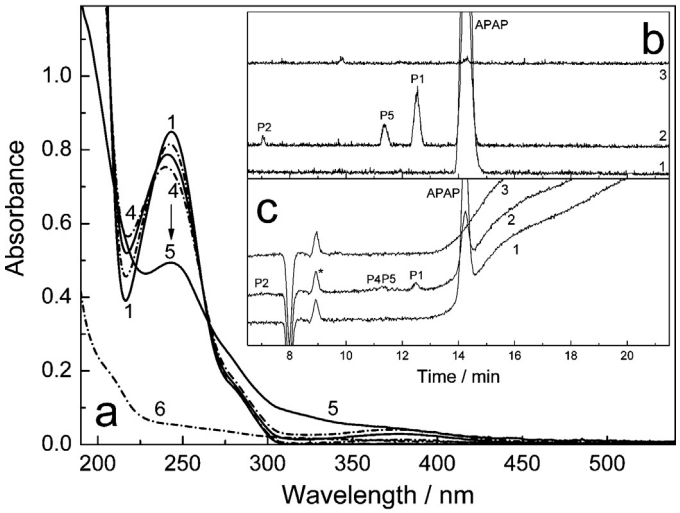


Fig. 5. Optical spectra (a) of air-saturated APAP (8.3×10^{-5} M) solution after 0 (1), 15 (2), 31 (3), 46 (4), 146 (5) and 280 (6) min of irradiation at 282 nm. The base peak (b) and UV (c) chromatograms after 0 (1), 46 (2) and 280 (3) min of irradiation, accordingly. *Impurity in the eluent. The energy of excitation was 1.2×10^{-3} E × l^{-1} × min^{-1}.

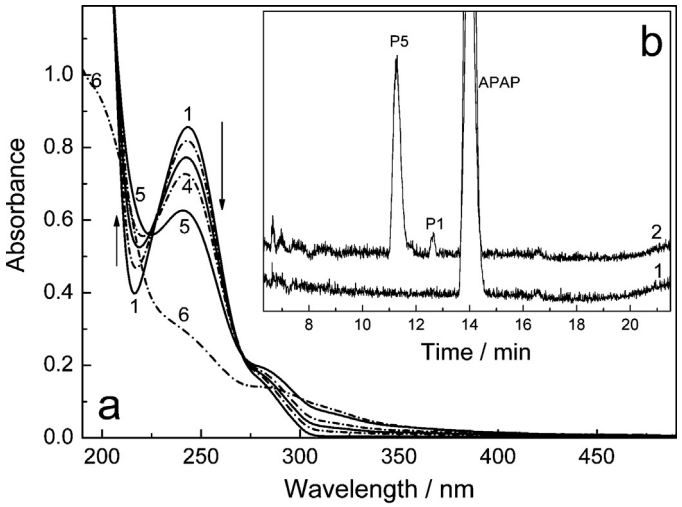


Fig. 6. Optical spectra (a) and base peak chromatograms (b) of irradiated at 266 nm air-saturated APAP (8.3×10^{-5} M) solution. (a) After 0 (1), 200 (2), 400 (3), 620 (3), 1060 (4) and 2400 (6) pulses. (b) After 0 (1) and 1060 (2) pulses. The energy of excitation was 70 mJ cm^{-2}.

groups were detected. So we assumed that **P4** is not the peroxyester but a ring-opened product (2E,4Z)-2-acetyl-3-amino-6-oxohexa-2,4-dienoic acid formed by oxidation of phenoxyl radicals derived upon **P1** photoionization by $O_2/O_2^{-\bullet}$. This assumption has to be proved by laser flash photolysis of **P1**. The mechanism of **P5** formation will be discussed later. Also two minor products (**P3** and **P6**) of APAP prolonged photolysis at 254 nm (Table 1) were detected by LC–MS. Both **P3** (*m*/*z* 274.070, $C_{14}H_{12}NO_5$) and **P6** (*m*/*z* 222.076, $C_{11}H_{12}NO_4$) exhibit similar fragment ions with characteristic mass losses of CH_2=C=O and several H_2O and CO molecules (Table 1S, Figs. 1S and 5S, ESI). **P6** was tentatively assign to 3-(3-acetyl-2-amino-5-hydroxyphenyl)-2-oxopropanal, the product of **P1** reaction with the fragment of oxidized aromatic ring of APAP (Fig. 6S and Table 1S, ESI). Unfortunately the existing MS/MS data for **P3** (Fig. 1S and Table 1S, ESI) could be assign to several possible chemical structures and the exact identification of **P3** seems to be impossible.

The excitation at 282 nm leads to APAP disappearance with the quantum yield $\varphi^{282} = 1.6 \times 10^{-3}$ which is equal to φ^{254} in the range of experimental error. The same main product **P1** and minor product **P2** as at 254 nm excitation were observed but also products with retention time 11.1 and 11.4 min (**P4** and **P5**) were formed (Fig. 5b and c). **P5** product clearly appears at early stage of photolysis when concentration of **P1** is negligible so its formation is not connected to **P1** photolysis and is due to photochemistry of APAP itself. It is worth to note that 282 nm excitation leads to faster decay of aromatic products (monitored by absorption at 250 nm) in comparison to 254 nm photolysis. The practically complete disappearance of aromatic products was observed after 280 min of irradiation at 282 nm (Fig. 5b, curve 3) though many peaks still present after 200 min of irradiation at 254 nm (Fig. 4b, curve 3).

The laser excitation at 266 nm (where two-photon ionization is the main process) leads to APAP disappearance with the quantum yield 0.013 which is practically one order higher than was observed at 254 or 282 nm excitation. The hydroxylated APAP, **P5** (*m*/*z* 168.066, $C_8H_{10}NO_3$, Table 1, Figs. 6b and 3S, ESI) is observed as the single main photoproduct. The formation of one predominant photoproduct is also confirmed by conservation of isosbestic points at 227 and 268 nm during initial stages of photolysis (Fig. 6a). This product most probably is formed by disproportionation of two phenoxyl radicals or reaction of phenoxyl radical with the superoxide radical anion (the product of the hydrated electron reaction with dissolved oxygen) [19]. The photo-Fries product is also formed (Fig. 6b and c) but as the quantum yield of photo-Fries reaction is $\cong 1.5 \times 10^{-3}$, **P1** is only minor product in these conditions.

The assignment of **P5** to the product of APAP photoionization gives evidence that such process plays role in APAP photochemistry under 282 nm light excitation too. It is worth to note that quantum yield of photo-Fries reaction at 282 nm is lower in comparison to 254 nm excitation as the overall quantum yield of APAP disappearance is practically the same at both wavelengths and the ratio of **P5**:**P1** is greatly increase at 282 nm photolysis.

Photolysis of synthesized **P1** product at 282 nm was also done in order to clarify nature and mechanism of APAP photoproducts formation. At the initial stages of **P1** photolysis no good isosbestic points and the formation of several photoproducts were observed (Fig. 7). One of the main photoproduct is the same as to be found at photolysis of APAP at 254 and 282 nm (**P4**, *m*/*z* 184.060, $C_8H_{10}NO_4$, Table 1). Other primary photoproducts of **P1** photolysis with retention time 18.0 (**S1**, *m*/*z* 287.141, $C_{16}H_{19}N_2O_3$) and 21.5 min (**S2**, *m*/*z*

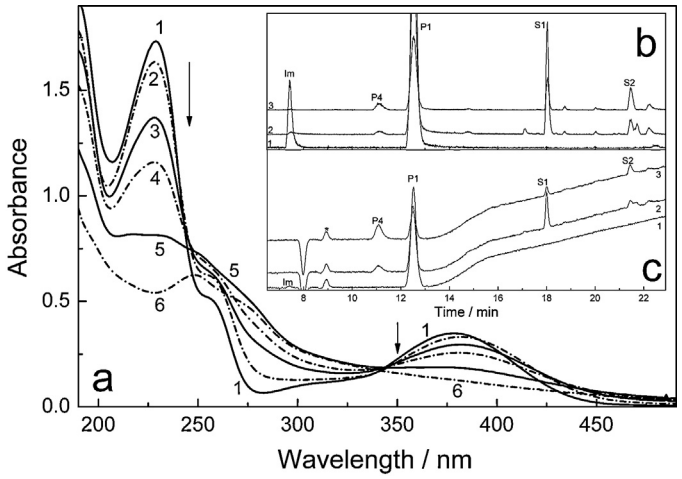


Fig. 7. Optical spectra (a) of air-saturated **P1** (1.05×10^{-4} M) solution after 0 (1), 12 (2), 23 (3), 40 (4), 73 (5) and 120 (6) min of irradiation at 282 nm. The base peak (b) and UV (c) chromatograms after 0 (1), 23 (2) and 73 (3) min of irradiation, accordingly. *Impurity in the eluent, "Im" C_8H_9NO, (*m*/*z* 136.076) the impurity in the synthesized **P1** compound. The energy of excitation was 1.2×10^{-3} E × l^{-1} × min^{-1}.

288.124, $C_{16}H_{18}NO_4$) were not observed at APAP photolysis (Table 1S, Fig. 7S and 8S, ESI). These dimeric products exhibit similar fragmentation picture and most probably are formed in reactions of some reactive intermediates with **P1** itself, as its concentration (10^{-4} M) was one order higher as one found in APAP photolysis experiments (10^{-5} M). For this reason the detailed identification of the structures of **S1** and **S2** was not done in this work.

3.3. Mechanism of APAP photolysis in the different experimental conditions

The results of steady-state and flash photolysis experiments allow us to make several conclusions concerning APAP photochemistry in aqueous solutions:

1. Laser excitation at 266 nm leads to predominant two-photon ionization of APAP with the formation of N-(3,4-dihydroxyphenyl)acetamide (hydroxylated APAP, **P5**) as the main photoproduct. The monophotonic ionization also takes place with the quantum yield about 10^{-3}.
2. Steady state photolysis of APAP at 254 nm leads to the formation of 1-(2-amino-5-hydroxyphenyl)ethanone (**P1**) as the main primary photo-Fries product (reaction (1)). **P5** photoproduct was detected at the prolonged irradiation of APAP at 254 nm and was not observed at steady-state photolysis of **P1**.
3. Steady state photolysis of APAP at 282 nm leads to the formation both **P1** and **P5** as the primary photoproducts clearly indicating the competition of two photochemical channels – photo-Fries reaction (**P1**) and monophotonic ionization (**P5**).
4. Prolonged UV irradiation of APAP at 254 nm and **P1** at 282 nm leads mainly to **P4** product formation.
5. The increase of photoionization quantum yield and the corresponding decrease of the photo-Fries reaction yield with increasing of excitation wavelength was observed.
6. Excitation at 282 nm is more favorable to the degradation of aromatic ring of APAP and its photoproducts in comparison to 254 nm excitation.

Based on aforesaid conclusions the following scheme of APAP photolysis was proposed (Fig. 8). Two different photochemical channels are reflecting dual nature of APAP molecule. On the one hand it exhibits properties of substituted acetanilides and undergoes photo-Fries reaction [17,18]. On the other hand APAP could be treated as substituted phenol and undergoes the photoionization in aqueous solution which is a typical process for phenols [22,27].

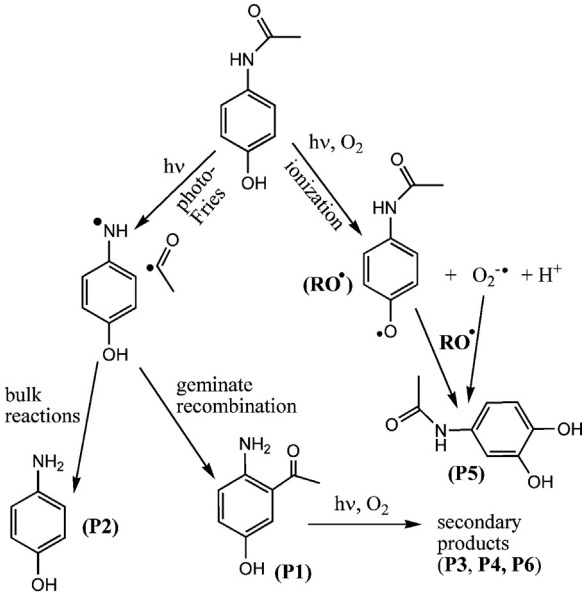


Fig. 8. The general scheme of APAP photolysis in aqueous solutions.

Most probably, the wavelength-dependent photochemistry of APAP could be explained by population of different excited states of molecule upon irradiation. Indeed, the UV absorption spectrum of APAP is typical for substituted acetanilides and consists of two overlapping bands assigned to $S_0 \leftarrow S_2$ ($\pi\pi^*$) (243 nm) and $S_0 \leftarrow S_1$ ($\pi\pi^*$) (≈280 nm) transitions (Fig. 1) [28,29]. It is known that photo-Fries reaction takes place in the picosecond time scale from the dissociative $\pi\sigma^*$ state populated by internal conversion from the lowest S_1 ($\pi\pi^*$) state [18,30]. Probably excess of excitation energy is favorable to the population of the dissociative $\pi\sigma^*$ state. In order to get deeper insight into the photochemistry of APAP one need to use the quantum chemical calculations.

4. Conclusions

In this work, mechanistic aspects of acetaminophen photochemistry in aqueous solution were investigated by combination of laser flash and steady-state photolysis with HPLC and LC–MS. Two competitive primary photoprocesses – photo-Fries reaction and photoionization were observed. The first processes dominates at short-wavelength (254 nm) excitation and leads to the formation of 1-(2-amino-5-hydroxyphenyl)ethanone (**P1**) as the main primary photo-Fries product. The photoionization is more important at long-wavelength excitation (282 nm) and leads to the formation of the single main product of phenoxyl radical reactions – N-(3,4-dihydroxyphenyl)acetamide (**P5**). Both photoprocesses have rather low quantum yields (about 10^{-3}). It was found that excitation at 282 nm is more favorable to degradation of aromatic ring of APAP and its photoproducts in comparison to 254 nm excitation. Nature of both primary and secondary photoproducts of APAP photolysis in different conditions was determined by LC–MS and the mechanism of wavelength-dependent APAP photochemistry was proposed and discussed. The results clearly show that both wavelength and light intensity could significantly influence on the phototransformation of APAP in aqueous solutions. The findings of this work also indicate that excimer UV lamps exhibit better performance to both APAP and its aromatic photoproducts removal than low-pressure Hg lamps.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2013.10.006.

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