# Radiolytic degradation of gallic acid and its derivatives in aqueous solution

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## ABSTRACT

Polyphenols, like gallic acid (GA) released in the environment in larger amount, by inducing some unwanted oxidations, may constitute environmental hazard: their concentration in wastewater should be controlled. Radiolytic degradation of GA was investigated by pulse radiolysis and final product techniques in dilute aqueous solution. Subsidiary measurements were made with 3,4,5-trimethoxybenzoic acid (TMBA) and 3,4,5-trihydroxy methylbenzoate (MGA). The hydroxyl radical and hydrogen atom intermediates of water radiolysis react with the solute molecules yielding cyclohexadienyl radicals. The radicals formed in GA and MGA solutions in acid/base catalyzed water elimination decay to phenoxyl radicals. This reaction is not observed in TMBA solution. The hydrated electron intermediate of water decomposition adds to the carbonyl oxygen, the anion thus formed protonates on the ring forming cyclohexadienyl radical or on the carbonyl group forming carbonyl centred radical. The GA intermediates formed during reaction with primary water radicals in presence of oxygen transform to non-aromatic molecules, e.g., to aliphatic carboxylic acids.

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## 1. Introduction

Plants, e.g., green tea or red grape, are rich natural sources of polyphenols, and they are commonly used as food additives and folk medicine [1]. The effects of these compounds are associated, to a great extent to their antioxidant properties, though other mechanisms may also be involved. The ability of polyphenols to protect cells from "oxidative stress" has been demonstrated. At the same time polyphenols exhibit a broad spectrum of other biological activities including anti-inflammatory, antivirial, antiatherogenic, antibacterial, as well as anticancer effects. A possible mechanism of polyphenol cytotoxicity may be related to their prooxidant properties, since the same polyphenol compound could behave both as antioxidant and prooxidant, depending on the concentration and free radical source [2].

Polyphenols released in the environment in larger amount may constitute environmental hazard. In slightly alkaline aqueous solutions in the presence of polyphenols, hydrogen peroxide can be formed: $H_2O_2$ may induce some unwanted oxidation in the nature, e.g., $SO_2 \rightarrow SO_3$, which increases the acidity of natural waters and contributes to "acid rain" [3]. The concentration of polyphenols in wastewater should be controlled.

Among the polyphenolic compounds gallic acid (3,4,5-trihydroxybenzoic acid, GA) and its derivatives constitute the most important group. Attached to the benzene ring GA contains a carboxylic group and three phenolic OH groups in 3, 4, and 5 positions. These groups undergo acid base equilibria with $pK_a$ of 4.4, 8.2, 10.7 and 13.1. The optical absorption spectrum of protonated GA in acidic solution exhibits a single absorption band at $\lambda_{max}$ 268 nm. The peak blue-shifts to $\lambda_{max}$ 259 nm with dissociation of the carboxyl proton (neutral solution). In slightly alkaline region, pH 8–11, there is a further dissociation at one of the phenolic OH groups yielding a dianion with $\lambda_{max}$ at 297 nm [4].

The wastewater of the wine and cork processing factories may contain GA derivatives in large amounts. In cork stopper factories the corkwood is immersed in boiling water for an hour for washing, the result is dark liquor which contains phenolic acids in high concentration [5,6].

The purification of wastewaters containing gallic acid and its derivatives by electrochemical processes, by photo activation or ozonization was studied previously [5,7–8]. Here we study the reactions during high energy irradiation. Ionizing radiations offer several advantages over the usual treatment methods (e.g., over $UV/H_2O_2$ technique): high energy irradiation treatment does not need additives, transparency and pH do not limit the treatment and the energy consumption is generally low. However, for practical applications detailed feasibility studies are needed to show the economical effectiveness.

Pulse radiolysis of GA and its derivatives was investigated several times in the past. O'Neill et al. [9] studied the radical

zwitterions formed in •OH radical addition in the acidic solutions to a large number of mono-, di- and trimethoxybenzoic acids, among them 3,4,5-trimethoxybenzoic acid (TMBA). Here there is no possibility for phenoxyl radical formation, the adduct undergoes $OH^-$ elimination yielding long lived zwitterion with negative and positive charge on the carboxyl group and on the ring. In the spectrum of TMBA •OH adduct there is a maximum at 390 nm with 6000 $mol^{-1}$ $dm^3$ $cm^{-1}$ molar absorption coefficient. The zwitterions formed in reaction with $H^+$ show a sharp absorption band around 300 nm and a wider one above 400 nm.

Richards and Adams [10] found two absorption bands in the spectrum of the transient formed in •OH + GA reaction: one around 400 nm and another at 325 nm. They identified the former as the transient absorption band of phenoxyl radical, since most of the phenoxyl radicals have characteristic band in this region [11]. According to their suggestion the 325 nm band belongs to the cyclohexadienyl radical forming in •OH addition to the ring.

The phenoxyl radical formed in one electron oxidation of GA with such oxidant radicals as $N_3^•$, $SO_4^{•-}$ and $B_2^{•-}$ exhibits a maximum around 310 nm and a shoulder at ~400 nm [12–14]. The spectrum of the phenoxyl radical formed from neutral MGA is similar to that of the GA. However, there is a well separated peak around 400 nm in the spectrum taken in ionized methyl gallate.

In this paper we report on the irradiation induced degradation of GA using both transient absorption spectroscopic (pulse radiolysis) and final product (UV spectroscopy, HPLC separation and UV detection) techniques. For deeper understanding of the transient kinetics we investigated the pulse radiolytic reactions of trimethoxygallate (TMBA) and methylgallate (3,4,5-trihydroxy methylbenzoate, MGA), as well. With this study we want to clarify some details of the radical scavenging reactions, and to contribute establishing irradiation technologies for wastewater purification.
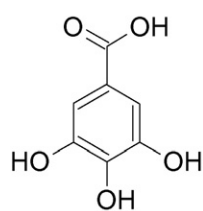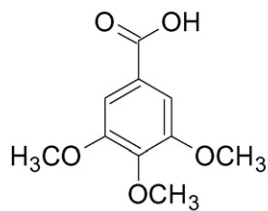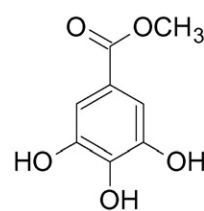


GA          TMBA          MGA

## 2. Experimental

GA, TMGA and MGA were purchased from Sigma–Aldrich and used as received. All chemicals were analytical grade. The pH of solutions was set by $HClO_4$ or NaOH. The aqueous solutions were prepared using Millipore deionized water.

In end product experiments the irradiation was done by $^{60}Co$ γ-irradiation facility with dose rates in the 1–9 kGy h$^{-1}$ range, or by a 4 MeV pulsed electron beam accelerator. The repetition of pulses was 50 Hz. The samples were evaluated either by taking UV–vis spectra using a JASCO 550 UV–vis spectrophotometer with 1 cm cell, or by HPLC separation and by detection using a diode array detector. Our chromatographic system consisted of a Jasco PU-2089Plus quaternary gradient pump, a Jasco MD-2015Plus diode array Multiwavelength Detector and Nucleosil 100 C18 5 μm, 15 × 0.4 cm$^2$ column (Technokroma®) [15]. The flow rate was 1 cm$^3$ min$^{-1}$ and the injection volume 20 mm$^3$. The solvents employed were 0.05 mol dm$^{-3}$ hydrochloric acid in water and methanol at isocratic elution gradient.

In pulsed radiolysis experiments, we used the same electron accelerator as in irradiation for end products. The investigations were carried out using 800 ns or 2.5 μs pulses of accelerated electrons, and an optical detection system with 2 cm pass-length [15].

All experiments were carried out at room temperature.

## 3. Results

### 3.1. Pulse radiolysis

#### 3.1.1. •OH radical reaction

During irradiation of aqueous solutions three transient radicals are produced from water decomposition: hydroxyl radical, hydrated electron, and hydrogen atom. Their yields are taken as 0.28, 0.28 and 0.06 μmol J$^{-1}$ [16]. In $N_2O$ saturated solutions due the $e_{aq}^- + N_2O + H_2O \rightarrow {}^•OH + e_{aq}^- + N_2$ transformation the reacting radicals and their yields are: hydroxyl radical 0.56 μmol J$^{-1}$, hydrogen atom 0.06 μmol J$^{-1}$. We studied the rate coefficient of the •OH + GA reaction by the build-up of absorbance in 3.5–12 pH range. In this range we measured the so-called diffusion controlled rate coefficient as $(1.2 \pm 0.15) \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$. The lack of pH dependence is simply due to the limitation by diffusion. Dwibedy et al. [13] and O'Neill et al. [9] published $1.1 \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $9 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ in the neutral and acidic pH ranges using also pulse radiolysis technique. Benitez et al. [5] obtained a similar value $(1.1 \pm 0.1) \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ by Fenton •OH generation and using competitive technique.

In the spectral studies with GA we set the pH to investigate the reactions of the neutral molecule, monoanion and dianion at pH 3.7, 6.8 and 9.7, respectively (Fig. 1). At these pH values two or three absorption bands with peaks between 300–350 and 350–450 nm were observed. However, the shapes of the bands, the places of the maxima and the changes of absorbances in time were strongly dependent on the pH.

At pH 6.8 the lower wavelength band was composed of two absorption peaks (Fig. 1A), at 310 and 340 nm. The 310 nm peak decayed quickly in time (see Inset), whereas the intensity of the 340 nm peak slightly increased in the time window of investigation. The longer wavelength band had maximum at 410 nm and the absorbance decreased to about its half during 140 μs.

At pH 3.7 there is no absorption peak at 310 nm (Fig. 1B). It may form, however its decay should be faster than 10 μs. The maximum of the low wavelength band is at about 340 nm, of the long wavelength band it is at 430 nm. Both bands are wide and structureless.

At pH 9.7 there is a peak at 335 nm, and a shoulder at 400 (Fig. 1C). The absorbance around 400 nm slightly decreases in time on the millisecond timescale.

In the spectrum of TMBA at pH 3.5 (Fig. 2A) we found the same absorption bands as in the case of GA: a band around 300–340 nm and a second one with maximum around 420 nm. The basic difference between the low pH spectra of TMBA and GA that in TMBA spectrum both bands decrease strongly and practically there is no compensation of the decrease of absorbance in time at 420 nm by the increasing absorbance at lower wavelength. At longer time there is an absorption band with maximum around 325 nm. This absorbance appears in most of the spectra measured here and it
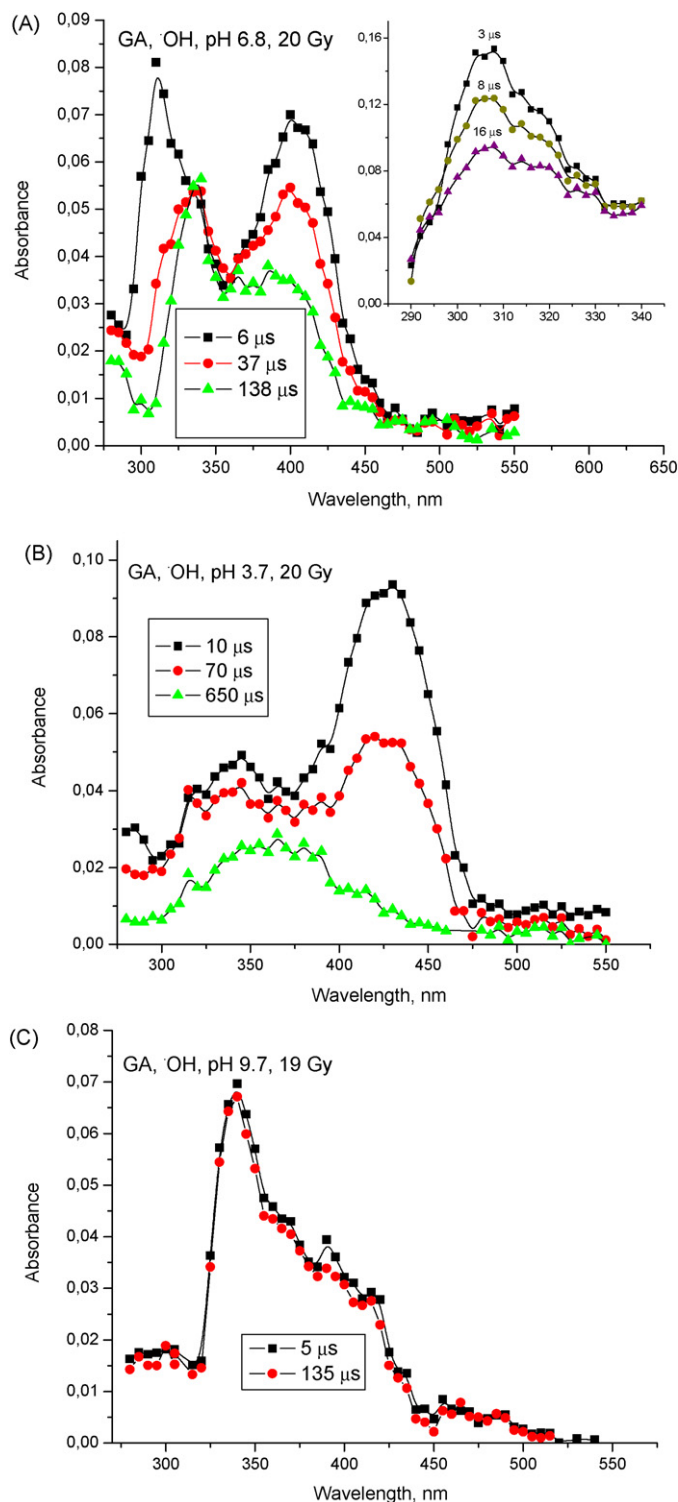
**Fig. 1.** Absorption spectra of intermediates formed in •OH radical + GA reaction at pH 6.8 (A), 3.7 (B) and 9.7 (C), respectively, taken in N₂O saturated 1 mmol dm⁻³ GA solutions. Inset of (A) shows the decay of the 310 peak on 10 μs timescale.

may be due either to a long living radical intermediate or to a final product. With TMBA the 420 nm absorbance is very strong even at pH 10.6 (Fig. 2B). This absorbance is certainly due to cyclohexadienyl radical that forms in •OH radical addition to the aromatic ring. Transformation of this radical to phenoxyl radical is highly blocked by the methyl substitution at the hydroxyl groups. The decay of the cyclohexadienyl radicals needs ~1 ms. The radical zwitterion,

studied by O'Neill et al. [9] in our system has low yield: it may give some contribution to the absorbance around 300 and 550 nm.

In the transient spectrum formed in methyl gallate + •OH reaction at pH 4.7 the shorter wavelength band is at 330 nm, the longer wavelength band has a maximum around 425 nm (Fig. 3A). The absorbance at 425 nm decreases on the 10 μs timescale, whereas the intensity of the 330 nm band remains essentially the same. This behaviour is similar to that observed for neutral GA at pH 3.7, in both cases the carboxyl group is non-ionized. Above the first ionization of MGA (p$K_a$ 8.03 [12]) at pH 10 there is a wide band between 350 and 450 nm, the shape of the spectrum does not change during the decay of several microseconds (Fig. 3B). This wide band in the 350–450 nm range resemble the phenoxyl radical absorption spectra of methyl-, bromo- and chloro substituted phenoxyl radicals [11,17]: at high pH the MGA spectrum also shows some structure. So the spectrum on Fig. 3B could belong to the phenoxyl radical of MGA.

### 3.1.2. H• atom reaction

The hydrogen atom reactions were studied by using the standard technique: N₂ saturated, moderately acidic solution (pH 2.2, in order to transform $e_{aq}^-$ to H• in reaction $e_{aq}^- + H^+ \rightarrow H•$) containing 5 vol.% tert-butanol (to convert •OH radicals to less reactive tert-butanol radicals). In the spectrum of Fig. 4 the 300–350 nm band is missing, there is only a wide band with $\lambda_{max}$ at 430 nm. The build-up of absorbance at 1 mmol dm⁻³ GA concentration needs a few μs.
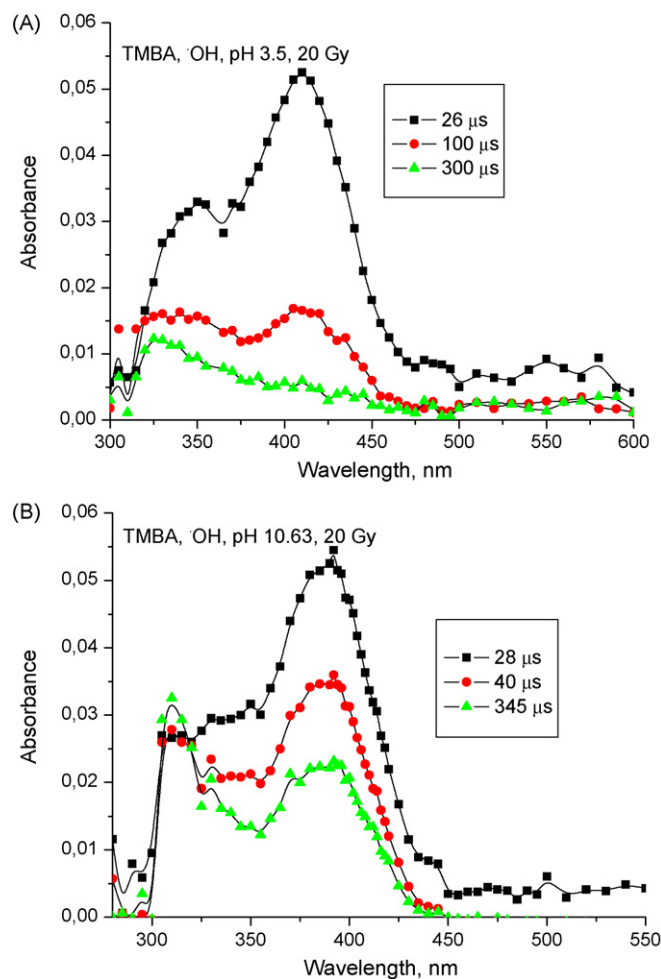


**Fig. 2.** Absorption spectra of intermediates formed in reaction between •OH radicals and 3,4,5-trimethoxybenzoic acid (1 mmol dm⁻³, N₂O saturated) at pH 3.5 (A) and 10.6 (B).
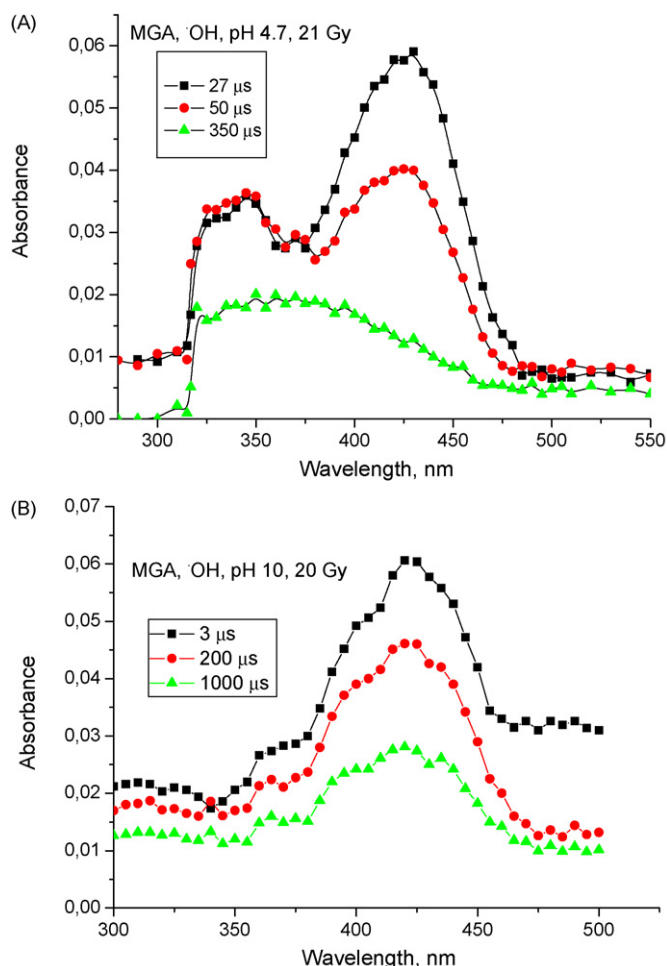
**Fig. 3.** Absorption spectra of intermediates formed in reaction between •OH radicals and methyl gallate (1 mmol dm$^{-3}$, N$_2$O saturated) at pH 4.7 (A) and 10 (B).

Assuming a 100% consumption of H• atoms in reaction with GA the molar absorption coefficient in the maximum is calculated to be c.a. 4500 mol$^{-1}$ dm$^3$ cm$^{-1}$. The second-order rate coefficient of the H• + GA reaction is around $5 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$. The absorbance decreased slowly: about 300 μs is needed to decrease c.a. by 80%. The decay is second-order with $2k \approx 1.5 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$.
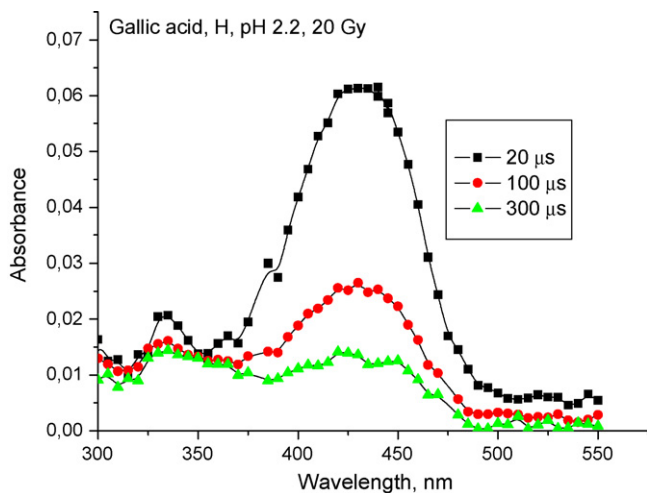


**Fig. 4.** Absorption spectra of intermediates formed in the reaction between H• atoms and GA in N$_2$ saturated pH 2.2, 1 mmol dm$^{-3}$ GA and 5 vol% *tert*-butanol containing solution.
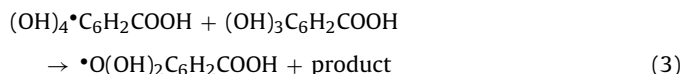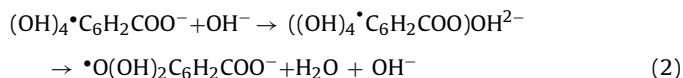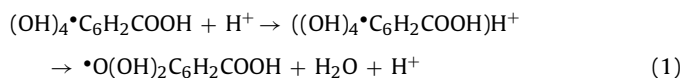
### 3.1.3. Identification of the absorptions bands of intermediates

In agreement with the suggestion of Dwibedy et al. [13] in the case of gallic acid the absorption band in the 350–450 nm range basically belongs to cyclohexadienyl radical, the peak in the 300–350 nm range is due to phenoxyl radical absorption. The invoked arguments are:

1. In the H atom adduct spectrum the 430 nm band is very strong (H atom adduct cyclohexadienyl radical), whereas the lower wavelength band is weak. The H atom adduct does not transform to phenoxyl radical.
2. The 300–350 nm band is weak in the transient spectrum of TMBA formed in •OH reaction. With this compound phenoxyl radical formation is highly hindered. The band also appears in the •OH reaction of MGA. In the latter case due to the presence of hydroxyl groups phenoxyl radicals can easily form.
3. In GA solutions the intensity of the 350–450 nm band decreases in the 10 μs timescale, the intensity of the 300–350 nm band increases or remains unchanged. This fact shows the conversion of the cyclohexadienyl radical to phenoxyl radical.
4. The absorption spectrum observed after the conversion in our studies is similar to the phenoxyl radical absorption spectrum obtained by direct oxidation [12–14].

### 3.1.4. Cyclohexadienyl radical → phenoxyl radical conversion

According to the classical work of Land and Ebert [18] the transformation of •OH adduct cycohexadienyl radical formed from phenol to phenoxyl radical takes place by an acid/base catalyzed reaction. Similar transformation mechanism was suggested for the hydroxyl radical adducts of a few other phenolic type compounds. In the case of *p*-cresol the rate coefficients of the
CH$_3$(OH)•C$_6$H$_4$OH + H$^+$(OH$^-$) → CH$_3$C$_6$H$_4$O• + H$_2$O + H$^+$(OH$^-$)
acid and base catalyzed reactions are $1.8 \times 10^8$ and $4.9 \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively [19]. As regards GA, Dwibedy et al. [13] suggested •OH adduct + GA reaction for this transformation. If the reaction takes place with acid/base catalyzed mechanism (reactions (1) and (2)) the transformation rate is strongly pH dependent, but independent of the GA concentration. The opposite is true for the •OH adduct + GA transformation mechanism (reaction (3)).

$$(OH)_4•C_6H_2COOH + H^+ \rightarrow ((OH)_4•C_6H_2COOH)H^+$$
$$\rightarrow •O(OH)_2C_6H_2COOH + H_2O + H^+ \tag{1}$$

$$(OH)_4•C_6H_2COO^- + OH^- \rightarrow ((OH)_4•C_6H_2COO)OH^{2-}$$
$$\rightarrow •O(OH)_2C_6H_2COO^- + H_2O + OH^- \tag{2}$$

$$(OH)_4•C_6H_2COOH + (OH)_3C_6H_2COOH$$
$$\rightarrow •O(OH)_2C_6H_2COOH + product \tag{3}$$

$$2(OH)_4•C_6H_2COOH \rightarrow (OH)_4C_6HCOOH + (OH)_4C_6H_3COOH \tag{4}$$

In our experiments we found pH dependence but independence from GA concentration, the result indicates again acid/base catalyzed reaction. If the base catalyzed reaction takes place with a similarly high rate coefficient as in the case of *p*-cresol, the cyclohexadienyl → phenoxyl transformation of GA at high pH needs a few μs. That is why we cannot see strong absorbance (cycohexadienyl radical) at pH 9.7 around 400 nm 5 μs after the pulse (Fig. 1C). The cyclohexadienyl → phenoxyl transformation is in competition with bimolecular reactions of cyclohexadienyl radicals (reaction (4)). The reaction can yield gallic acid derivative with four OH groups attached to the ring (2,3,4,5-tetrahydroxy benzoic acid). The
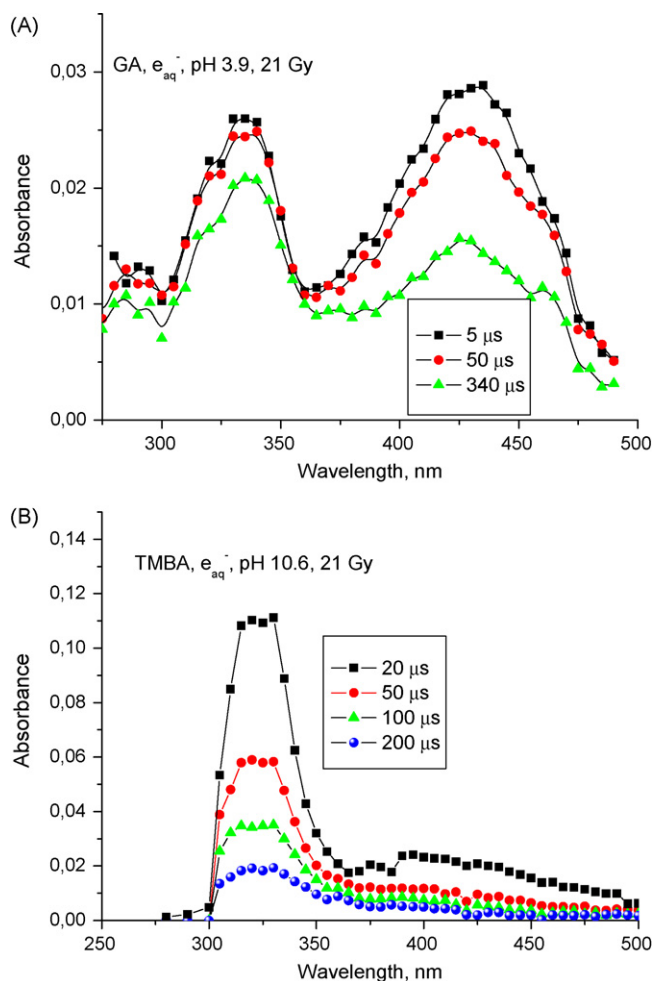
(A) GA, $e_{aq}^-$, pH 3.9, 21 Gy

— 5 µs
— 50 µs
— 340 µs

(B) TMBA, $e_{aq}^-$, pH 10.6, 21 Gy

— 20 µs
— 50 µs
— 100 µs
— 200 µs

**Fig. 5.** Absorption spectra of intermediates formed in the reaction between $e_{aq}^-$ and GA (1 mmol dm$^{-3}$) at pH 3.9 (A) and between $e_{aq}^-$ and TMBA (1 mmol dm$^{-3}$) at pH 10.6 (B), in N$_2$ saturated, 5 vol% *tert*-butanol containing solutions.

compound may have somewhat different absorption spectrum as the starting compound GA.

### 3.1.5. $e_{aq}^-$ reaction

The reaction of hydrated electron with GA was studied at pH 3.9 in N$_2$ saturated 5 vol.% *tert*-butanol containing solution. In the absorption spectra there are two bands with maxima at 340 and 435 nm (Fig. 5A). At 5 µs the two bands have nearly identical intensities, however, the longer wavelength band decays faster than the shorter wavelength band, indicating that these two bands belong to two different intermediates.

Dwibedy et al. [13] also reported $e_{aq}^-$ adduct spectrum for gallic acid. They observed a similar longer wavelength band as we found, however they did not identify the peak. When we make a possible identification we should take into account that the longer wavelength band shows similarities to the absorption band of the cyclohexadienyl radical that forms in H$^\bullet$ atom addition reaction.

The reaction between $e_{aq}^-$ and benzoic acid was investigated in several publications and the absorption bands in the spectrum were identified. Both in GA and benzoic acid the $e_{aq}^-$ would enter the lowest vacant molecular orbital available which might be considerably delocalized due to the overlap of the π systems of the aromatic ring and the carboxylic side chain [20]. In case of benzoic acid this electron capture is followed by a protonation (pK$_a$ 5.3), the protonation is suggested to take place on the carboxylic moiety. The intermediate has an absorption band between 290 and
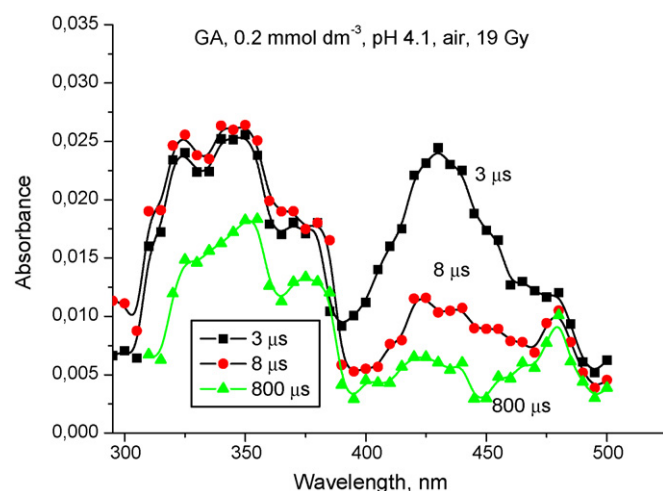


GA, 0.2 mmol dm$^{-3}$, pH 4.1, air, 19 Gy

— 3 µs
— 8 µs
— 800 µs

**Fig. 6.** Absorption spectra taken in air saturated 0.2 mmol dm$^{-3}$ GA solution at natural pH.

340 with maximum at 335 nm. We assume that in the case of the GA pK$_a$ is lower due to the three electron donating OH groups. The lower wavelength band is probably due to the radical formed by protonation at the carboxylic group (reaction (6)). The higher wavelength band seems to be due to an H$^\bullet$-atom adduct that forms in protonation at the ring (reaction (7), cyclohexadienyl radical).



(5)



(6)



(7)
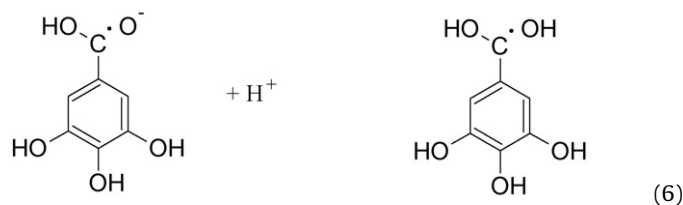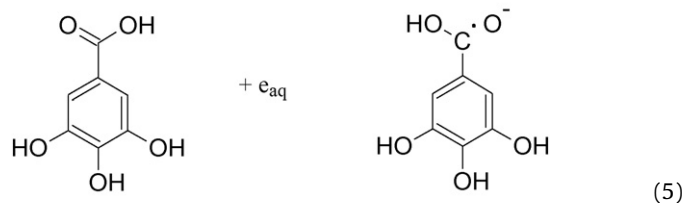
This identification gains support from the measurements made with TMBA (Fig. 5B). At high pH in the absorption spectrum of intermediate formed in reaction between $e_{aq}^-$ and TMBA we see only the low wavelength peak. The molar absorption coefficient for this peak is calculated to be in the order of $1.5 \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$. For benzoic acid the absorption coefficients of intermediates with radical sites on the carboxyl group and on the ring are $(1.5–2.5) \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$ and $(3–4) \times 10^3$ mol$^{-1}$ dm$^3$ cm$^{-1}$ (Simic and Hofmann, 1972). As it was mentioned before the H atom adduct of GA (cyclohexadienyl radical) has a molar absorption coefficient of c.a. 4500 mol$^{-1}$ dm$^3$ cm$^{-1}$.

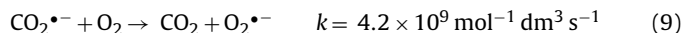### 3.1.6. Experiments in the presence of air

In Fig. 6 we show the spectrum taken in 0.2 mmol dm$^{-3}$ air saturated GA solution at natural pH (~4.1). Due to the low solute

concentration, $H^\bullet$ and $e_{aq}^-$ practically entirely react with $O_2$, therefore $^\bullet OH$ radicals and the $HO_2^\bullet/O_2^{\bullet-}$ pair ($pK_a$ 4.8) are the possible reactive intermediates. We have to note that $O_2^{-\bullet}$ has low reactivity with GA (rate coefficient $3.4 \times 10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$), and the reactivity with $HO_2^\bullet$ is probably even lower, in the reaction phenoxyl radical formation is expected [12]. The spectrum is more complicated than a simple $^\bullet OH$ adduct spectrum, showing increased number of transients. At this pH both the neutral and the singly ionized forms are present in comparable concentration. The absorbance around 430 nm is observed in the $^\bullet OH$ adduct spectrum taken in $N_2O$ saturated solution, as well, and belongs to the cyclohexadienyl radical absorption. The intensity of this peak decreases quickly and that of the wide absorption band in the 300–400 nm region (phenoxyl radical) slightly increases. Similar behaviour was observed in $N_2O$ saturated solution. Based on the similarity of the spectral changes in $N_2O$ and air saturated solutions we suppose that the intermediate radicals are not very much sensitive to $O_2$ at this pH. There are also differences between the spectra taken in air saturated and $N_2O$ saturated solutions. In air saturated solution the intensity is much smaller than in $N_2O$ saturated solution; this is due to the smaller $^\bullet OH$ radical yield (0.28 and 0.56 $\mu$mol J$^{-1}$).

### 3.2. Steady-state degradation experiments

Fig. 7 shows the absorption spectra of air saturated un-irradiated and electron beam (A) or gamma (B) irradiated 1 mmol dm$^{-3}$ GA solutions at pH 3.7. Because of the high absorbance in the UV region before the spectrophotometric measurements we applied 10 times dilution. The intensity of the 240–310 nm absorption band (characteristic to aromatic ring) decreases with the dose: at 20 kGy the decrease is c.a. 40–70%. A weak new band appears with maximum around 290–310 nm. The absorbance curves cross each other at about 307 nm, however, as the higher resolution spectra have shown, there is no real isosbestic point here. At higher doses in the 240–310 nm region there is no well defined absorption peak, which shows complete destruction of the aromatic structure. The structureless absorbance may be due to a large number non-aromatic product.

As mentioned in Section 3.1.6, in air saturated solution a part of the hydrated electrons and $H^\bullet$ atoms reacting with dissolved oxygen transforms to the $HO_2^\bullet/O_2^{\bullet-}$ pair. The low reactivity of the pair with GA is also evident from the degradation experiments we made in oxygen saturated 0.05 mol dm$^{-3}$ sodium formate containing solution. In such solution through the reactions:

$$HCO_2^- + {}^\bullet OH \rightarrow CO_2^{\bullet-} + H_2O \qquad k = 3.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad (8)$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^{\bullet-} \qquad k = 4.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad (9)$$

$^\bullet OH$ is also converted to superoxide radical anion. The moderate decrease observed in HCOONa solution in addition to the $HO_2^\bullet/O_2^{\bullet-}$ reaction with GA, partly can also be due to a not complete scavenging of water radiolysis intermediates by $O_2$ or HCOO$^-$ and their reaction with GA.

As the insets in Fig. 7 show the efficiency of GA degradation is slightly higher in the absence of oxygen than in its presence. In $N_2O$ saturated solution, when through $^\bullet OH$ radicals, cyclohexadienyl and phenoxyl radicals are produced there is a strong decrease of the GA concentration with the dose: the logarithm of absorbance decreased linearly with the dose that is generally observed in hydroxyl radical reactions [21]. The radical–radical reactions of cyclohexadienyl and phenoxyl radicals lead to destruction of the aromatic rings (initial yield $G \approx 0.1$ $\mu$mol J$^{-1}$). In $N_2$ saturated solution the decomposition may take place through $^\bullet OH$ adduct cyclohexadienyl radicals, phenoxyl radicals, $H^\bullet$ adduct cyclohexadienyl radicals and intermediates with radical sites on the carboxyl group. The efficiency is similar in $N_2O$ and $N_2$ saturated
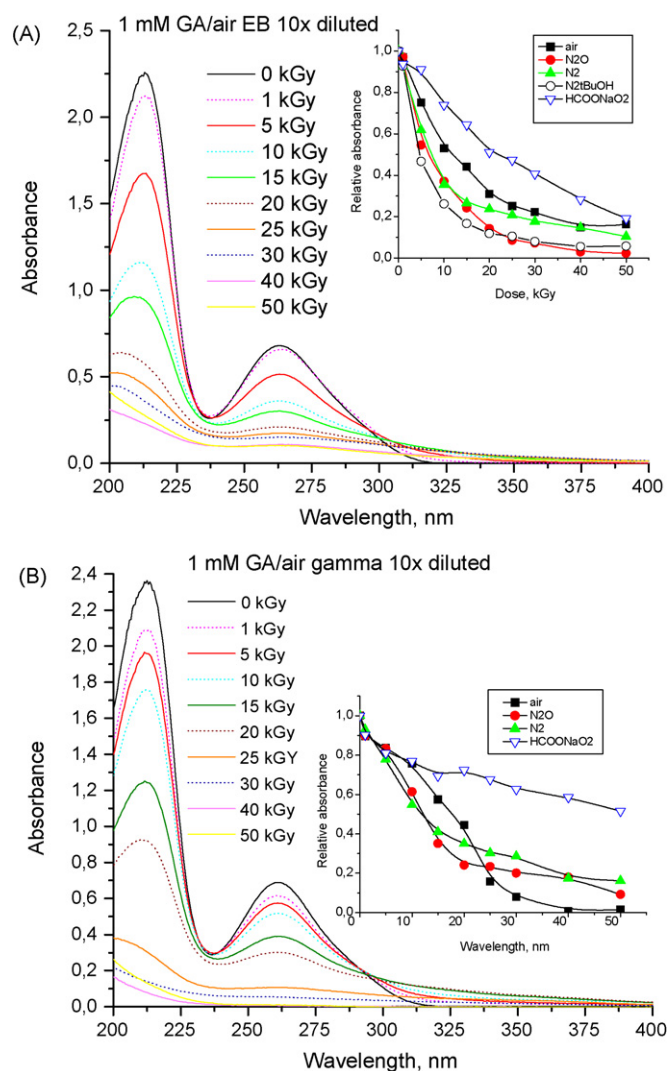


**Fig. 7.** Absorption spectra of air saturated un-irradiated and EB (A) or gamma (B) irradiated 1 mmol dm$^{-3}$ GA solutions. Before taking the spectra the solutions were 10 times diluted. Insets: relative absorbance measured at 265 nm as a function of dose.

solutions up to 15 kGy, above this dose the efficiency in $N_2$ saturated solution is smaller. Decrease of the reactivity with increasing dose is observed when the reactivity of the water radiolysis intermediates with product molecules is higher than with the starting compound. In Fig. 7A we show also the degradation in *tert*-butanol containing $N_2$ saturated solution: the sharp decrease shows the high efficiency of hydrated electrons in destructing GA molecules.

We investigated the product formation by EB irradiating the solutions with increasing doses up to 84 kGy. As the 3D plot in Fig. 8 shows we obtained a good HPLC separation of GA and its products. The GA is eluted at 7.6 min and the three main radiolytic products (RPI, RPII and RPIII) have retention times of 3.9, 4.8 and 5.6 min, respectively.

The relative integrated absorbancies (normalized to the maximum integrated absorbance) of GA and those of the main products RPI, RPII and RPIII are shown as a function of dose in Fig. 9A. Based on the absorption spectra in Fig. 9B we can conclude that the products are not aromatic molecules. This finding is in agreement with the work of Boye et al. [7], who in electrochemical oxidation under conditions where $^\bullet OH$ radicals are the main reacting species identified aliphatic (oxalic, malic, formic, maleic and fumaric) acids as products of oxidation. Due to the formation of acids we found a
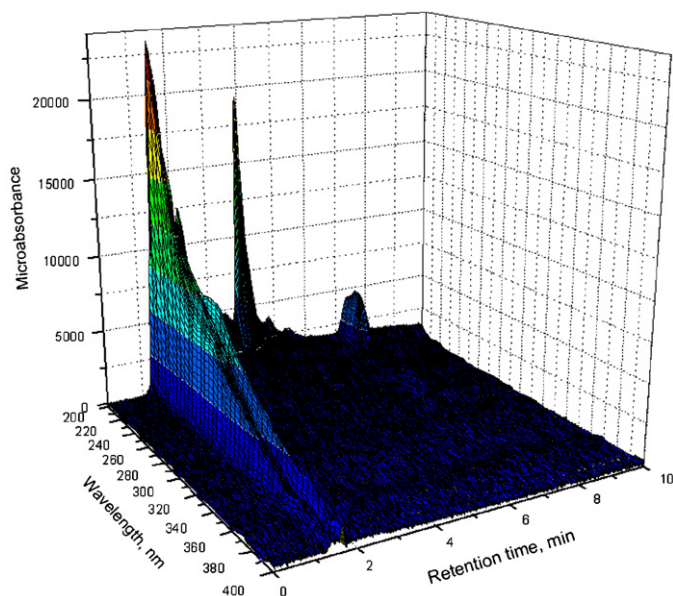
**Fig. 8.** HPLC 3D chromatogram of 1 mmol dm$^{-3}$ GA aqueous solution, pH 3.1 irradiated at 360 kGy/h dose rate with 48 kGy dose.

gradual decrease of the pH with the dose in air saturated solutions: in 1 mmol dm$^{-3}$ unbuffered solution the pH decreased from ca. 3.7 to 3.2 after 40 kGy absorbed dose.

In Fig. 9A, the RPIII formation starts at small doses, the curve goes over a maximum at ~6 kGy. The formation curve of RPII has a
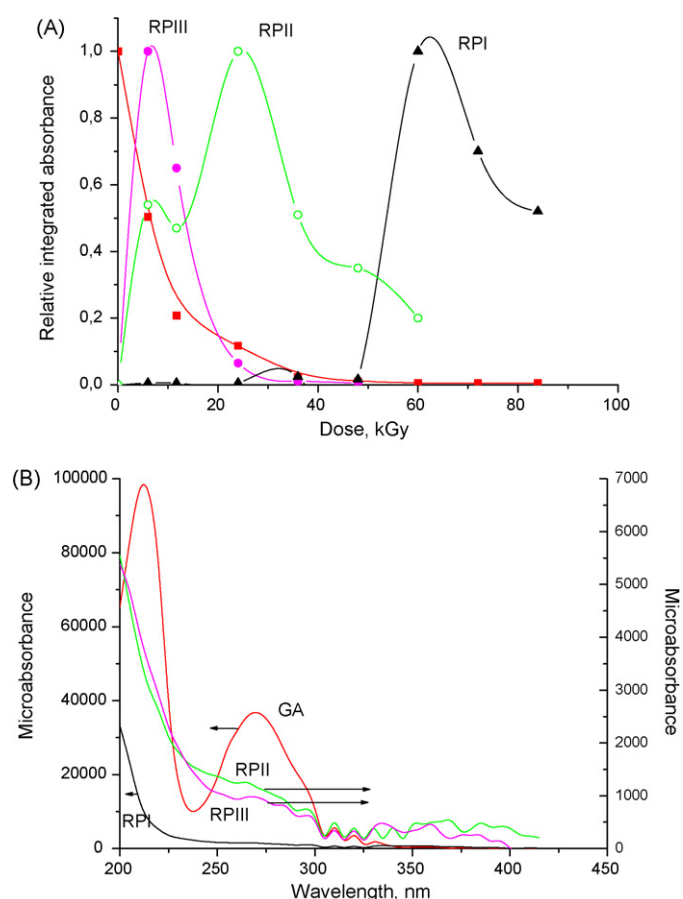


**Fig. 9.** Dose dependencies of integrated absorbancies of GA, RPI, RPII and RPIII (A) and their absorption spectra obtained in HPLC separation (B).

maximum at ~24 kGy. Although there is a larger delay in the formation of RPI, the maximum is at about ~58 kGy. The decay of GA and the formation of RPII and RPIII show some parallelism, however, the formation of RPI may be connected with the decay of formation of RPIII. Therefore, RPI is probably due to a secondary decomposition.

We repeated the degradation experiments by setting the pH to 7. In N$_2$O and N$_2$ saturated solutions at higher pH we found somewhat smaller degradation efficiencies than at lower pH. In air saturated solution, however, higher efficiency was measured at high pH indicating more effective reaction between oxygen and the intermediates of GA decomposition. No pH dependency was found in solutions containing HCOONa. At lower pH reaction between HO$_2$$^{\bullet}$ and GA, at the higher between O$_2$$^{\bullet-}$ and GA monoanion is expected, the results suggest low rate coefficients for both reactions as suggested [12].

## 4. Conclusion

Based on pulse radiolysis studies performed with GA, TMBA and MGA we conclude that hydroxyl radical reacts with the solute molecules yielding cyclohexadienyl radicals with light absorption in the 350–450 nm wavelength range. In GA and MGA solutions in acid/base catalyzed water elimination reaction the cyclohexadienyl decays to phenoxyl radical with absorption maximum in the 300–350 nm range. In the case of TMBA the cyclohexadienyl radical → phenoxyl radical transition is blocked since no water elimination could take place. In the reaction of hydrogen atoms cyclohexadienyl radicals are produced. The hydrated electron gets scavenged on the carbonyl oxygen. In the subsequent protonation carbonyl centred or ring centred (cyclohexadienyl) radicals are produced.

In 1 mmol dm$^{-3}$ GA solution 30–50 kGy dose is needed to destroy the aromatic structure, at lower concentrations proportionally lower doses are required. The efficiency of degradation of the aromatic structure is similar in $^{\bullet}$OH and e$_{aq}$$^{-}$ reactions. In air saturated solution it is somewhat smaller than in the absence of oxygen. In degradation of gallic acid aliphatic carboxylic acids form as indicated by the decrease in pH.

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