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Radiation induced degradation of organic molecules: relation between chemical structure and degradability in advanced oxidation processes

PhD Theses

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1. Introduction, aim of the research work

The topic of the dissertation has been investigated for more than 15 years in the Radiation Chemistry Department of the Institute: it is related to environmental protection. Nowadays one of the most important environmental challenges is the preservation of the quality of drinking water. Soil and drinking waters are contaminated, because of the rapid growth of the population, and the large-scale development of agriculture and the industry. The concentration of organic pollutants (especially the drugs and their metabolites) detected in surface waters is growing. Their natural degradation requires long time and these chemicals can accumulate in the food chain. New technologies are under development for the demolition of these compounds in aqueous media.

In the last two decades several laboratories started developing new, highly effective techniques for water purification. They are called advanced oxidation processes (AOP). These new methods have a common feature: they apply reactive compounds/intermediate products such as O_3 , $\cdot OH$, $H\cdot$, $HO_2\cdot$ to degrade organic compounds. High-energy irradiation technology, which belongs also to AOP processes, produces reactive intermediates (radicals) during the radiolysis of water.

In the first part of our work, we illustrate our degradation techniques on the examples of some pharmaceutical molecules. The main compound we investigated in this part was diclofenac. It is a relatively complicated molecule containing two differently substituted benzene rings. It was obvious to examine the two parts separately with suitable model compounds. One of the model compounds was 2,6-dichloroniline which is the main degradation product of diclofenac. The other was paracetamol, which is a widely used pharmaceutical compound and its degradation had been studied in several AOP. Both the basic/initial molecule and its degradation products are soluble in water.

The intermediates were studied using pulse radiolysis, while the degradation was followed by UV-VIS spectroscopy, separation by HPLC and products identification by diode array and MS-MS detection. The effect of dose, atmosphere, and additives were investigated. The chemical oxygen demand, the total organic carbon content and the toxicity of the solutions were also studied.

In the second part of the work, the relationship between the chemical structure and the degradability was investigated by measuring the chemical oxygen demand (COD) values on more than 20 compounds. In laboratory experiments reported in the literature the oxidation of many organic compounds was studied, however, very few works reported on the comparison

of their oxidative degradability. Here the radiation induced degradation of a large number of aromatic molecules is studied investigating the degradation efficiency – molecular structure relationship by precisely measuring the chemical oxygen demand (COD) values.

2. Literature Overview

Although several studies have already been published on the degradation of drug molecules in aqueous solution under irradiation by ionizing radiation, these processes have been studied much less than degradation by other AOP methods. The degradation of diclofenac and paracetamol molecules have been already studied in several AOP, but no publication was found on its radiation induced degradation^{1,2}. Although, there are studies on the degradation of chloroanilines as studied by pulse radiolysis and also by gamma radiolysis^{3,4}, no studies report on the identification of its final products.

The research in this field mainly focuses on following the disappearance of the initial molecules, or identifying some of the final products. In the decompositions induced by different methods (eg. UV photolysis, Fenton, photo-Fenton), the intermediate are often the same and this is the case with the final products formed. However, by using these techniques 100% mineralization have never or very rarely been reached⁵.

In the case of diclofenac, it was concluded that both ring have been degraded, but the degradation of the ring containing chlorine is slower than that of the other ring. By ozone oxidation and UV/H₂O₂ treatment it has been observed, that the chlorine was degraded to

¹ Pérez-Estrada, L. A.; Malato, S.; Gernjak, W.; Agüera, A.; Fernandez-Alba, A. R. Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway. *Environ. Sci. Technol.*, **2005**, *39*, 8300-8306.

² Dalmázio, I., Alves, T.M.A., Augusti, R. An appraisal on the degradation of paracetamol by TiO₂/UV system in aqueous medium. Product identification by gas chromatography-mass spectrometry GC-MS. *J. Braz. Chem. Soc.*, **2008**, *19*, 81-88.

³ Lichtscheidl, J.; Getoff, N. Radiolysis of halogenated aromatic compounds in aqueous solutions-I. Conductometric pulse radiolysis and steady-state studies of the reactions of e_{aq}⁻. *Int. J. Radiat. Phys. Chem.*, **1976**, *8*, 661-665.

⁴ Sánchez, M.; Wolfger, H.; Getoff, N. Radiation-induced degradation of 4-chloroaniline in aqueous solution. *Radiat. Phys. Chem.*, **2002**, *65*, 611-620.

⁵ Andreozzi, R.; Caprio, V.; Marotta, R.; Vogna, D. Paracetamol oxidation from aqueous solution by means of ozonation and H₂O₂/UV system. *Water Res.*, **2003**, *37*, 993-1004.

chloride ion⁶. During the degradation process diclofenac-2,5-iminokinon, 5-hydroxy-diclofenac and 2,6-dichloroaniline have been identified as primary decomposition products⁷.

In treating acetaminophen by TiO₂/UV method, hydroquinone, monohydric paracetamol and aliphatic carboxylic acid (fumaric acid, maleic acid)⁸ were identified as final products by the GC-MS method.

When using ozonization and H₂O₂ photolysis treatment, it was found that both oxidative systems can degrade the aromatic ring. The efficiency of the mineralization is 30 - 40%. Using pulse radiolysis, Bisby and Tabassum studied the reaction between •OH and paracetamol. The absorption band in the transient absorption spectrum with wavelength greater than 400 nm, was attributed to the phenoxy radical. This radical was very often observed by the EPR technique, in the EPR studies it is called iminoquinone radical⁹. The name is used to indicate that the unpaired electron can be located either on the oxygen or on the nitrogen atom, although the latter seems more likely.

The expectations against the new technologies are high. Apart from being economic, another main objective is that the method should be effective over a wide range of contaminants, and that the technology should be relatively simple, and should achieve high efficiency at low energy consumption. Additional requirement is that the technology should require only a limited number of chemical additives, and the final degradation products should be non-toxic. As it is obvious from our studies also, these requirements can be easily met by using irradiation technology for water purification.

The radiolysis of water gives a distribution of transient and stable products according to equation (1). The values in brackets are the yields, the so-called G-values in $\mu\text{mol J}^{-1}$ units. In order to study the reactions of the three reactive intermediates separately ($\bullet\text{OH}$, e_{aq}^- and $\text{H}\bullet$) different additives and techniques are applied¹⁰. In N₂O saturated solutions due to the (2) transformations the reacting radicals and their yields are: hydroxyl radical 0.56 $\mu\text{mol J}^{-1}$, hydrogen atom 0.07 $\mu\text{mol J}^{-1}$. The reactions of hydrated electron can be studied in N₂

⁶ Coelho, A. D.; Sans, C.; Agüera, A.; Gómez, M. J.; Esplugas, S. Effect of ozone pretreatment on diclofenac: intermediates, biodegradability and toxicity assessment. *Sci. Total Environ.*, **2009**, *407*, 3572-3578.

⁷ Sein, M. M.; Zedda, M.; Tuerk, J.; Schmidt, T. C.; Gollach, A.; Von Sonntag, C. Oxidation of diclofenac with ozone in aqueous solution. *Environ. Sci. Technol.*, **2008**, *42*, 6656-6662

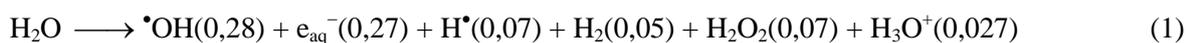
⁸ Andreozzi, R.; Caprio, V.; Marotta, R.; Vogna, D. Paracetamol oxidation from aqueous solution by means of ozonation and H₂O₂/UV system. *Water Res.*, **2003**, *37*, 993-1004.

⁹ Bisby, R. H.; Tabassum, N. Properties of the radicals formed by one-electron oxidation of acetaminophen-a pulse radiolysis study. *Biochem. Pharmacol.*, **1988**, *37*, 2731-2738.

¹⁰ Wojnárovits, L. Sugárkémia. Akadémiai Kiadó, Budapest, **2007**.

saturated, 5 vol% *tert*-butanol containing solutions. In such solution the $\bullet\text{OH}$ radicals react with *tert*-butanol forming rather inactive *tert*-butanol radicals (3).

In air saturated solutions due to the low solute concentration applied, $\text{H}\bullet$ and e_{aq}^- practically entirely react with O_2 , therefore $\bullet\text{OH}$ radicals and the $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ pair ($\text{pK}_a = 4.8$) are the possible reactive intermediates. The pair have low reactivity with aromatic compounds¹¹.



3. Methodology

The degradation of the molecules (diclofenac, paracetamol, 2,6-dichloroaniline) was studied by using two methods: gamma and pulse radiolysis. We carried out the gamma radiolysis experiments with + PBq (1600 TBq) activity of ^{60}Co γ -source.

The pulse radiolysis is a unique tool for creating $\bullet\text{OH}$ radicals and other strong oxidants in water medium and for studying their reactions. The technique uses short pulse of accelerated electrons. It triggers the production of reactive intermediates, radicals and ions¹². In the present work the reactions of hydroxyl radical and the selected molecules (2,6-dichloroaniline, paracetamol) were studied. The solutions were bubbled with nitrous oxide.

The intermediates were studied using pulse radiolysis, while the degradation during gamma radiolysis was followed by UV-VIS spectroscopy, separation by HPLC and products identification by diode array and MS-MS detection. The effects of dose, irradiation atmosphere and additives were investigated. The chemical oxygen demand, the total organic carbon content and the toxicity of the solutions were also studied.

The **chemical oxygen demand** (COD) means the amount of O_2 molecules needed for the oxidation of dissolved and suspended organic matters in unit volume of water (mg dm^{-3}).

¹¹ Jovanovic, S. V.; Hara, Y.; Steenken, S.; Simic, M. G. Antioxidant potential of gallic catechins. A pulse radiolysis and laser photolysis study. *J. Am. Chem. Soc.*, **1995**, *117*, 9881-9888.

¹² Földiák G.; György I.; Hargittai P.; Wojnárovits L. A kémia legújabb eredményei: A szénhidrogének impulzusradiolízise. Akadémia Kiadó, Budapest. **1991**.

COD is one of the most important features of wastewater samples¹³. COD value of the untreated and treated wastewater samples provides information about the extent of degradation of organic matter that has taken place during the oxidation¹⁴.

The efficiency of radiation induced oxidation (E) is characterized here by the ratio of the number of O₂ molecules built in the products and the number of water radicals (R[•]) introduced in the system:

$$E = \frac{\Delta\text{COD}/\text{dose}}{3,2 \cdot 10^7 G(\text{R}^\bullet)\rho} \quad (1)$$

where $\Delta\text{COD}/\text{dose}$ is in $\text{mg dm}^{-3} \text{ kGy}^{-1}$, ρ is the density in kg dm^{-3} . The efficiency values based on oxygen uptake measurements (published in the literature for some compounds) are also shown in Table 1 calculated as the ratios of the reported G(oxygen consumption) values and the yield of hydroxyl radical formation, G([•]OH) (both in mol J^{-1}).

Determination of the **total organic carbon** (TOC) content is applied by different research areas. The TOC analysis is suitable for investigating the content of organic matter in wastewater and its chemical characterization.

It is essential that the treated water leaving the wastewater plant has low **toxicity**. Thus, studies have not only taken into account the degradation level of organic compounds (COD, TOC), but toxicity levels were also studied. The toxicity was investigated by using luminescent bacteria. The increasing luminescence indicates lower toxicity¹⁵.

Irradiation induced changes were evaluated by **HPLC** separation. Two HPLC systems were used. In System 1 the separation was on Nucleosil 100 C18 5 μm , $15 \times 0.4 \text{ cm}^2$ column (Technokroma®) with Jasco MD-2015Plus diode array detection. In System 2 the samples were analysed by an Agilent Technologies 6410 Triple Quad LC/MS equipment. Both mass spectrometric (total ion and selective ion monitoring) and diode array detections were applied. Separations were made with a C18 column.

In the second part of the work, as it was already mentioned, the relationship between the chemical structure and the degradability was investigated by measuring the COD values on

¹³ Nagy szerves anyag tartalmú szennyvizek KOI értékeinek meghatározása - mérési leirat a *ISO 6060:1991* szabvány szerint

¹⁴ Pisarevsky, A. M.; Polozova, I. P.; Hockridge, P. M. Chemical Oxygen Demand. *Russ. J. App. Chem.* **2005**, *78*, 101-107.

¹⁵ Farré, M.; Ferrer, I.; Ginebreda, A.; Figueras, M.; Olivella, L.; Tirapu, L.; Vilanova, M.; Barceló, D. Determination of drugs in surface water and wastewater samples by liquid chromatography-mass spectrometry: methods and preliminary results including toxicity studies with *Vibrio fischeri*. *J. Chromatogr. A*, **2001**, *95*, 187-197.

more than 20 compounds. We started our experiments with the simplest aromatic hydroxy compound, the phenol. Investigation of the phenol and its sodium salt was followed by examination of cresol isomers. These molecules contain a hydroxyl and a methyl group on the ring. The experiments were widened by involving chloro- and aminophenols. In case of these disubstituted methyl, amino and chloro phenols the reactions of all the three isomers (*ortho*, *meta*, *para*) were investigated. Finally, the irradiation of more complex, heavily substituted compounds were performed: 2,4-D, aspirin, ketoprofen, Acid Red 1, DCF, 2,4-dichloroaniline, acetovanillone, gallic acid. Measurements were also carried out with the non-aromatic maleic and fumaric acids.

4. Results

The degradation of the three molecules (diclofenac, 2,6-dichloroaniline, paracetamol) was studied by two methods: gamma and pulse radiolysis. The effects of dose, irradiation atmosphere and additives (N_2O , $N_2 + t$ -butanol, N_2 , air) were investigated. Irradiations under different conditions helped to identify the intermediates. However, from the point of view of the wastewater treatment investigations on aerated solutions are of predominant importance. The radiation chemistry of the three model compounds shows some similarities, but we found several differences, too.

Here I show the evaluation of the pulse radiolysis results on the example of paracetamol: Fig. 1. shows the transient spectra in N_2O saturated $5 \times 10^{-4} \text{ mol dm}^{-3}$ solution.

The transient absorption spectrum obtained in $\bullet OH$ reaction with paracetamol shows three bands: one of them is between 300 and 350, the other one is between 350 and 400 nm, and third one is around 440 nm. Based on literature analogies, in the transient spectrum (in Fig. 1) the band between 350 and 400 nm is due to the absorbance of dihydroxycyclohexadienyl radical which forms when the hydroxyl radical reacts with aromatic rings partially saturating one of its double bonds. At shorter wavelengths the intensity decreases with time, while at long wavelengths, the absorbance stays unchanged or slightly increases. It is likely that the intermediate product absorbing in the 350 - 400 nm range is being transformed to the intermediate product absorbing around 440 nm. The latter band is typical for the phenoxy type radicals. As it was mentioned before, in the EPR literature this radical is called iminoquinone radical.

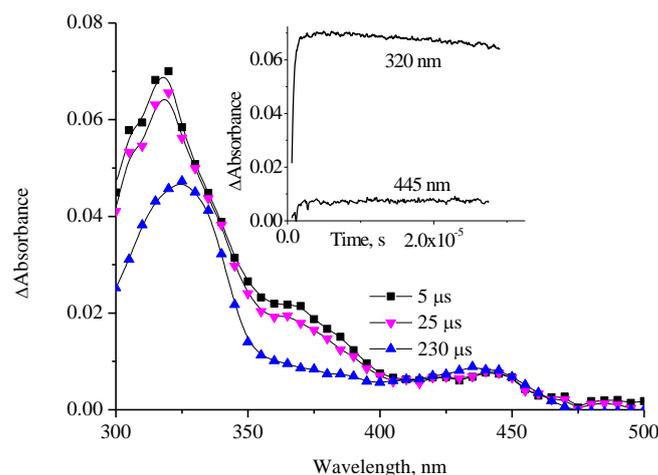


Fig. 1. Transient spectra in N_2O saturated $5 \times 10^{-4} \text{ mol dm}^{-3}$ paracetamol solution ($\bullet\text{OH}$ reaction). Inset: transient signals at 320 and 445 nm. Dose/pulse 19 kGy.

Hydroxyl radical may also react with 2,6-DCA and diclofenac forming cyclohexadienyl radical. These radicals have longer lifetime, than the carbon centered radicals formed in paracetamol. The rate coefficients were calculated based on the kinetic curves recorded at the absorption maximum of the intermediate products spectra. The rate coefficient values for the three molecules are slightly different: 2,6-DCA $3,5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, paracetamol $7,7 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and DCF $9,5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The reason for the relatively small value for 2,6-DCA is the two electron withdrawing chlorine atoms on the aromatic ring, which decrease the rate of electrophilic reaction. In the case of DCF the reaction with the ring containing electron-donating groups is the preferred. With 2,6-DCA such a reaction can also be detected, in which the $\bullet\text{OH}$ abstracts a hydrogen atom from the amino group, in the reaction meanwhile anilino radical is being formed.

Radiation chemical decomposition products were published for the first time for these three compounds. During irradiation formation of several new compounds was observed in the case of all three molecules, among them products hydroxylated on the aromatic ring formed with high yield confirming data obtained by pulse radiolysis studies showing the attack of hydroxyl radical on the aromatic ring. These products were also observed in other AOP's (O_3 , Fenton reactions, $\text{H}_2\text{O}_2/\text{UV}$). This can be explained by the fact that $\bullet\text{OH}$ radical was the reactive intermediate in all cases. The yield of the phenolic products is the highest in the air saturated solutions. It can be concluded that the dissolved oxygen promotes the phenol formation and also contributes to the ring opening reactions. The generally un-reactive $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$

intermediates, which are always present in aerated solutions, also have contribution to the degradation processes, but it is of low importance.

During irradiation the changes in chemical oxygen demand and total organic carbon content, in case of using sufficiently high dose, demonstrated the total decomposition of all three compounds, i.e., mineralization of the molecules.

Upon irradiation of solutions of all three compounds, the COD values decreased nearly linearly with the increasing dose up to 20 – 30 kGy (5×10^{-4} mol dm⁻³ concentration), indicating step-by-step oxidation. However, the measured COD/dose values indicate different oxidation rates. At 30 kGy dose the COD values of diclofenac, 2,6-DCA and paracetamol are 20, 62 and 75 percent of the initial values, respectively. In 2,6-DCA and DCF solution after the linear period the COD values decrease slower. This behavior is typical of aromatic molecules because during the mineralization the hydroxycyclohexadienyl type radicals, which are generated in the reaction of the $\bullet\text{OH}$ radicals, react with dissolved oxygen readily. The peroxy radicals can initiate the opening of the ring. In these reactions carboxylic acids form, which are not easily degradable by irradiation. In contrast to the previous observations (and to the compounds have been investigated in our laboratory so far) in case of paracetamol the rate of the COD decrease became faster after the linear period. Accordingly, it can be concluded that the initial decomposition products can be degraded easier than the paracetamol itself.

TOC was also determined for all three compounds: in all cases TOC decreased more slowly with the increasing dose than COD. The reason behind this phenomenon is the identical amount of carbon atoms in the first intermediates and the starting material. However, due to oxidation, the oxygen-carbon ratio is higher in the first intermediates than in starting molecules.

Measurements on toxicity of paracetamol and diclofenac showed that the changes in toxicity during irradiation are highly dependent on the toxicity of the starting material: if the original molecule is of high toxicity, during irradiation a decrease in toxicity can be observed in the initial period of degradation. If high doses were used, toxicity could be completely eliminated.

The rate constant for the reaction between e_{aq}^- és DCF is $(1,68 \pm 0,05) \times 10^9$ dm³ mol⁻¹ s⁻¹. Reactions of hydrated electron and hydroxyl radical resulted in different products. The nucleophilic e_{aq}^- may attack the aromatic ring possessing two electron withdrawing chlorine substituents, which is followed by the chloride ion elimination. The radicals formed may give products with quinone structure.

The rate constant for the reaction between e_{aq}^- and paracetamol was found to be $5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The lower rate constant is probably due to the presence of the two electron donating substituents on the ring, which make unfavorable the attack of the nucleophilic hydrated electron. Since the rate constant of the $e_{aq}^- + \text{paracetamol}$ reaction is low, while that of the $e_{aq}^- + \text{O}_2$ reaction is high, in air saturated samples the $e_{aq}^- + \text{paracetamol}$ reaction does not take place. During pulse radiolysis experiments only spectra of poor quality were obtained. The weak absorbance is most probably the consequence of the slow reaction: the majority of e_{aq}^- react with other radiolysis intermediates instead of paracetamol.

In the reaction between hydrated electron and 2,6-DCA in the intermediate spectra also unusually low absorbances were obtained, which make the identification of intermediates extremely difficult. Radicals having cyclohexadienyl structure may form by e_{aq}^- addition to the ring followed by protonation. As it is usual in case of aromatic rings substituted with halogen atom(s), e_{aq}^- may bind to the halogen atom, and the adduct may decompose to chloride ion and phenyl radical. The latter is of high reactivity, and attack the *tert*-butanol, resulting in the formation of 2-hydroxy-2,2-dimethyl-ethyl radical, that absorbs light of wavelength shorter than 300 nm. The phenyl radical may also give cyclohexadienyl radicals by radical addition pathway.

Relation between chemical structure and degradability

In the first part of the thesis the reactions between hydroxyl radical and three model compounds were studied and rate constants were found to be of the same order of magnitude for the three molecules. At the same time by COD measurements significantly different rates of oxidation reactions were found. The degradation rate molecular structure relationship investigation studies were extended to more than 20 compounds.

The tested compounds are summarized in Table 1 together with the concentration applied, the theoretical and measured COD value, the slope of regression ($\Delta\text{COD}/\text{dose}$), its standard deviation ($(\sigma) \text{ mg dm}^{-3} \text{ kGy}^{-1}$) and the oxidation efficiencies (E (equation 2.1)).

When planning the experiments we had to consider not only the optimal concentration range (200 and 600 mg dm^{-3}) needed for high accuracy of COD measurements, but also other factors, e.g. the solubility.

The *o*-. *m*-. *p*-aminophenol and *N*-(4-hydroxyphenyl)acetamide (paracetamol) solutions had $1 \times 10^{-3} \text{ mol dm}^{-3}$ initial concentrations. The $\Delta\text{COD}/\text{dose}$ values obtained are 4.7 ± 0.7 , 3.5 ± 1.0 , 5.0 ± 0.9 , $3.7 \pm 1.2 \text{ mg dm}^{-3} \text{ kGy}^{-1}$.

No	Comopund	Concentration mol dm ⁻³	COD _{meas} /COD _{theor}	Slope, (ΔCOD/dose) mg dm ⁻³ kGy ⁻¹	E
1	Phenol	2 × 10 ⁻³	453/448	8.8±0.6	0.98
2	Na Phenolate (pH 10,5)	5 × 10 ⁻³	1120/1120	18	2
3	<i>o</i> -Cresol	1.5 × 10 ⁻³	395/408	8.6±0.6	0.96
4	<i>m</i> -Cresol	1.5 × 10 ⁻³	439/408	8.5±0.3	0.95
5	<i>p</i> -Cresol	1.5 × 10 ⁻³	377/408	7.6±0.8	0.85
6	<i>o</i> -Clorophenol	2 × 10 ⁻³	418/432	8.0±0.8	0.89
7	<i>m</i> - Clorophenol	2 × 10 ⁻³	442/432	7.1±0.6	0.79
8	<i>p</i> - Clorophenol	2 × 10 ⁻³	410/432	9.4±0.4	1.05
9	2,4- Dichlorophenoxy -acid (2,4-D)	2 × 10 ⁻³	441/496	8.0±0.5	0.9
10	Aspirin	1.5 × 10 ⁻³	401/432	8.1±0.5	0.9
11	Ketoprofen	4 × 10 ⁻⁴	222/230	9.0±1.0	1
12	Acid Red 1	1.5 × 10 ⁻³	840/850	5.5±0.8	0.61
13	<i>o</i> -Aminophenol	1 × 10 ⁻³	216/208	4.7±0.7	0.52
14	<i>m</i> -Aminophenol	1 × 10 ⁻³	213/208	3.5±1.0	0.39
15	<i>p</i> -Aminophenol	1 × 10 ⁻³	216/208	5.0±0.9	0.55
16	Paracetamol	1 × 10 ⁻³	253/272	3.7±1.2	0.4
17	DCF	5 × 10 ⁻⁴	230/236	9.0±0.3	1
18	2,6-DCA	5 × 10 ⁻⁴	89/91	5.5±1.0	0.61
19	Acetovanillone	5 × 10 ⁻⁴	153/160	6.9±0.4	0.77
20	Gallic acid	2 × 10 ⁻³	340/384	8.5±0.8	0.95
21	Maleic acid	4 × 10 ⁻³	374/384	7.4±0.7	0.82
22	Fumaric acid	4 × 10 ⁻³	411/384	9.0±0.7	1

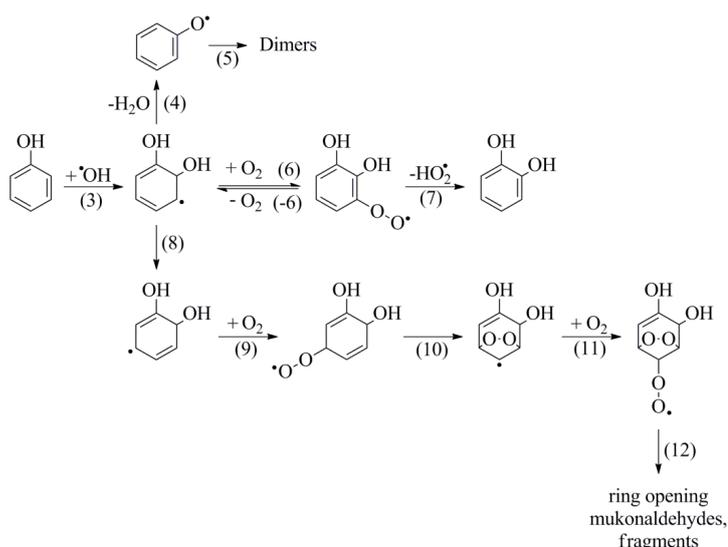
Table 1. Chemical oxygen demand values (COD) and oxidation efficiencies (E).

The ΔCOD/dose of *p*-aminophenol solution with 1.5 × 10⁻³ mol dm⁻³ concentration was 4.6 ± 0.8 mg dm⁻³ kGy⁻¹. Diclofenac was investigated at 1.5 × 10⁻³ mol dm⁻³ concentration, and 9.0 ± 0.3 mg dm⁻³ kGy⁻¹ was found for ΔCOD/dose.

By the ratio of the decrease of COD and the amount of reactive water radiolysis intermediates introduced into the system the oxidation efficiencies were calculated. The efficiency values (E) were found to be around 0.2 - 1 (O₂ molecule built in the products/[•]OH).

In the next paragraph we will explain the reason of the big differences found between the E values for different molecules. It will be also explained what it means that the one electron oxidant [•]OH performs a 2 - 4 electron oxidations.

E around 1 shows that the one electron oxidant $\bullet\text{OH}$ induces four electron oxidations. The mechanism of degradation is presented on the example of phenol (figure on the right).



$\bullet\text{OH}$ is suggested to add to phenol in *ortho*-, or *para*-positions. In Scheme 2 *ortho*-addition is shown (Reaction (1)). The

hydroxycyclohexadienyl radicals produced in (1) may undergo water elimination yielding phenoxy radical (2). Phenoxy radicals are suggested to decay in dimerization reactions (3). As a result of this reaction sequence the chemical oxygen demand for the new compounds is smaller than for the starting molecules: one $\bullet\text{OH}$ attack decreases the amount of O_2 needed for oxidation by $1/4$ O_2 molecule (one electron oxidation). This reaction does not cause any change in dissolved oxygen concentration.

The hydroxycyclohexadienyl radical may react with dissolved O_2 in (4) to form peroxy radical in a reversible process. The O_2 addition reaction is fast, the adduct is relatively stable when electron donating substituent is attached to the ring; the opposite is true for electron withdrawing substituent. With phenol the reversible reaction is strongly shifted towards the peroxy radical formation. When the O_2 adduct in (5) eliminates an $\text{HO}_2\bullet$ two-electron-oxidized phenol molecule (here catechol) is obtained; with this product an $\bullet\text{OH}$ attack reduces the oxygen demand by $1/2$ O_2 molecule.

In phenol the decay of the peroxy radical is dominated by the $\text{HO}_2\bullet$ elimination. However, the hydroxycyclohexadienyl radical in (6) may undergo a rearrangement to a semiquinone type radical. The intermediate is capable of taking-up two O_2 molecules, after reacting with the first O_2 in (7) the peroxide intermediate undergoes isomerization (8) to endoperoxide, and then the carbon centered radical thus formed in (9) reacts with O_2 . Degradation of this latter intermediate is suggested to lead to mukonic acid and aldehyde derivatives and smaller molecular mass organic molecules. It is evident that if the latter reaction route is dominating E can be 1 or higher. Based on the efficiency values close to 1 determined for many of phenolic type compounds studied here, we assume that reactions (6) to (10) play important role in degradation.

The efficiencies for the phenol molecules containing amino or acetamide group (*o*-, *m*-, *p*-aminophenol and *N*-(4-hydroxyphenyl)acetamide) are rather low (0.4 - 0.5). The $\bullet\text{OH}$ induced transformations of aminophenols, especially that of *p*-aminophenol, were investigated in several pulse radiolysis experiments and fast formation of the aminophenoxy or anilino radicals was observed. The $\text{O}_2 +$ hydroxycyclohexadienyl radical reaction probably cannot compete effectively with hydroxycyclohexadienyl radical transformation to phenoxy or anilino radicals. The fast formation of the latter radicals reduces the rate of oxidation.

E is lower (0.61) for the complicated dye molecule Acid Red 1 than for the other aromatic molecules. Here $\bullet\text{OH}$ has several preferred places to attack the molecule, among others it may attack the azo group. The hydrazyl type radical thus formed does not react with O_2 .

In the case of diclofenac, which has an -NH- group between two aromatic rings, E is high, 1.0. The main $\bullet\text{OH}$ induced degradation of the molecule starts with $\bullet\text{OH}$ addition to the ring without Cl-atom substituent. The subsequent reactions may partly be similar to the ones discussed for phenol.

Conclusion: The value of E is high, when the one electron oxidant $\bullet\text{OH}$ performs 2 - 4 electron oxidations in dissolved-oxygen containing solutions, such as in the cases of phenol, cresols, maleic acid and fumaric acid. On the contrary, E is small when amino, acetamide or hydrazo group is attached to the phenol ring, so when one $\bullet\text{OH}$ performs one- or two-electron oxidations. The resulting transient products (phenoxy, anilino, semiiminoquinon, hidazil radicals) react with oxygen slowly resulting in a less efficient decomposition.

5. Theses

1. Hydroxyl radical very effectively degrades aromatic molecules. In pulse radiolysis experiments the structure of the transient intermediates, in end product experiments, after ^{60}Co γ irradiations, the aromatic decomposition products were determined. According to the transient absorption spectra obtained in pulse radiolysis, the hydroxyl radical mainly attacks the aromatic rings. [H2, H3, H4].

2. The change of toxicity during radiolysis is mainly determined by the toxicity of the starting compound. In case of investigation of a highly toxic compound, with increasing dose a decreasing toxicity was observed. When the investigated molecule was of low toxicity, the

intermediates had higher toxicity, than the starting material, thus an increasing toxicity was experienced.

Among the investigated molecules diclofenac is of moderate, while paracetamol is of low toxicity. In case of these molecules the formation of rather toxic intermediate products was established (for diclofenac 2,6-dichloro aniline, for paracetamol hydroquinone and acetamide) at low doses [H2, H3].

3. HPLC techniques can be applied successfully for separation and identification of decomposition products obtained by radiolysis of diclofenac or paracetamol solutions performed under different conditions. In the reaction of diclofenac and hydroxyl radical the main products were the dichloroaniline and hydroxylated diclofenac. If the same compound reacts with e_{aq}^- three products could be determined: 4-chloroaniline, dichloroaniline and a third compound possessing quinone structure. When air saturated paracetamol solutions were irradiated, the main products were the two isomers of hydroxyparacetamol [H2, H3].

4. Based on the examination of more than 20 compounds it was established, that in the range of the concentration applied (4×10^{-4} - 5×10^{-3} mol dm⁻³) the COD values decrease nearly linearly with the increasing dose up to 20 - 30 kGy. Above this dose limit the dose dependence of the COD values deviated from linear, usually the efficiency of degradation was lower. This phenomenon can be explained by formation of oxidized, non-aromatic molecular fragments (acids, aldehydes), because their reactions with $\cdot\text{OH}$ are very slow [H1, H5, H6].

5. It was established, that the efficiency of oxidation (E) strongly depends on the structure of the radicals formed during hydroxyl radical reactions. The E value is high, when the one electron oxidant $\cdot\text{OH}$ induces 2 - 4 electron oxidations in dissolved-oxygen containing solutions, such as in the cases of phenol, cresol, or maleic and fumaric acid. On the contrary, E is small when amine, acetamide or hydrazo group is attached to the phenol ring (one $\cdot\text{OH}$ performs one- or two-electron oxidations). The resulting intermediate products (phenoxy, anilino, semiiminoquinon, hidazil radicals) react with oxygen slowly resulting a less efficient decomposition [H5, H6].

6. Expected impact and further research

Due to Human activity, a large amount of man-made non-degradable organic compounds pollute our environment and surface water. The organic compounds (such as the environmentally hazardous drug molecules) could be easily degraded by applying irradiation technology, which at the same time can guarantee disinfection as well. This technology is not yet introduced in Europe in industrial scale. In semi-industrial scale the technology is already used in many countries around the world (USA, Brazil, Korea, China, etc). In Korea and in China the wastewater treatment using electron accelerator technology has already been implemented on an industrial scale, combined with the conventional wastewater treatment. Based on the results and experiences, the EB treatment is concluded to be economical. Therefore, we recommend using radiation technology to treat wastewater polluted by bacteria and organic compounds (such as pharmaceuticals) also in the European countries.

7. Papers related to the Thesis

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