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# Ionizing radiation induced degradation of monuron in dilute aqueous solution



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## HIGHLIGHTS

- Hydroxycyclohexadienyl type radicals form in reactions of hydroxyl radical.
- Dechlorination takes place in reactions of hydrated electron and hydroxyl radical.
- Hydrated electron also induces ring degradation.
- Presence of chlorine atom increases the efficiency of decomposition.
- Based on calculations *para*-reaction is highly favoured in hydroxyl radical reaction.

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## ABSTRACT

The decomposition of monuron was investigated in dilute aqueous solutions using pulse radiolysis and  $\gamma$ -radiolysis in order to identify the intermediates and final products. The main reaction takes place between monuron and the hydroxyl radicals yielding hydroxycyclohexadienyl type radicals with a second order rate constant of  $(7.4 \pm 0.2) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . In  $\cdot\text{OH}$  reactions, the aminyl and phenoxy radicals may also form. Dechlorination was observed in both hydroxyl radical and hydrated electron reactions. The  $\cdot\text{OH}$  induced dechlorination reactions are suggested to occur through OH substitution or phenoxy radical formation. The rate of oxidation is very high in the presence of dissolved oxygen. Some of the results are also supported by quantum chemical calculations.

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## 1. Introduction

Pollution of surface waters and waste waters by herbicide residues constitutes a very serious environmental problem. Entering the environment these herbicides are highly persistent and their biodegradation is very slow. They reach the aquatic environment via leaching or runoff processes from soils. Among herbicides, phenylurea herbicides are applied in significant amount in both agricultural and non-agricultural fields. Some of them (monuron and linuron) may be carcinogenic for humans (Ragsdale and Menzer, 1989). The phenylurea herbicides do not have UV–vis light absorption above 300 nm, therefore, their photodegradation is very slow (Brahmia et al., 2002). Several Advanced Oxidation Processes (AOPs) were tested and recommended for their degradation.

The present target of investigations, monuron (3-(4-chlorophenyl)-1,1-dimethylurea), belongs to this class of herbicides. Its decomposition was studied e.g. in photolysis (Nélieu et al., 2008; Canle López et al., 2001; Canle López et al., 2005), in electro-Fenton (Oturán et al., 2010), in photo-Fenton (Bobu et al., 2006), in  $\text{H}_2\text{O}_2$  photolysis (Bobu et al., 2006), in photocatalytic (Bobu et al., 2006; Mešt'ánková et al., 2004; Chu and Rao, 2012), in photo-induced Fe(III) reactions (Mešt'ánková et al., 2004) or in ozonation experiments (Tahmassebi et al., 2002). During direct photolysis, decomposition of monuron was very slow similarly to the other phenylurea herbicides. In all the other AOPs, the degradation of monuron was attributed to the reactions of hydroxyl radicals, as a result of OH-attack N-demethylation on side chain, hydroxylation or OH substitution of a chlorine atom on aromatic ring take place. In the previous studies, photo-Fenton reaction has proved to be the most effective method for decomposition of monuron with 90–100% efficiency of removal. In these reactions hydroxylated,

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N-demethylated or dechlorinated products formed. Searching the literature we did not find work on the radiolytic degradation of this compound, however, the high energy radiation induced degradations of diuron and fenuron have already been studied (Zhang et al., 2008; Kovács et al., 2014, 2015).

In this study, decomposition of monuron was investigated with high energy irradiation technique and the intermediate radicals were observed with pulse radiolysis under different conditions. The final products formed in  $\gamma$ -irradiated air saturated samples were also identified. Finally, quantum chemical calculations were applied to support the interpretation of our experimental results on the aromatic ring hydroxylation.

## 2. Materials and methods

### 2.1. Chemicals and equipment

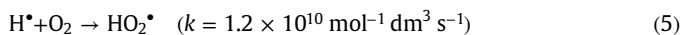
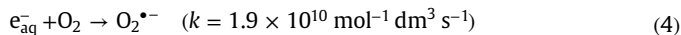
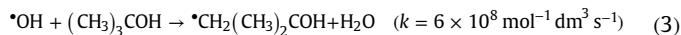
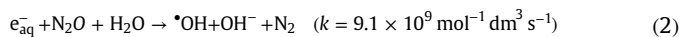
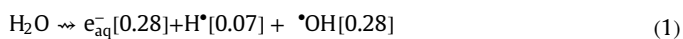
Monuron and other chemicals were purchased from Spectrum-3D or Carlo Erba and used without any purification. All solutions were prepared without any buffer addition and pH adjustment. The samples before and after irradiation by a Co-60 gamma source were characterized by JASCO 550 UV-vis spectrophotometer with a 1 cm cell applying appropriate dilutions before taking the spectra. Agilent Technologies 6410 Triple Quad LC/MS system was used for final products identification. The concentration of adsorbable organic halides (AOX) and free chloride ions in solutions were monitored by an AOX equipment and perfectION™ Combination Chloride Electrode, respectively. Other comprehensive characteristics of the solution, such as Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Nitrogen (TN) contents were also measured using Behrotest TRS 200 COD system and Shimadzu TOC-VCSN equipment, respectively.

The computational analysis was performed using Density Functional Theory (DFT) methods. Becke's (1993) three parameter hybrid functional was used with the Lee–Yang–Parr correlation extension, generally known as B3LYP. The standard 6–311G++(d,p) (McLean and Chandler, 1980; Krishnan et al., 1980; Clark et al., 1983; Frisch et al., 1984) basis set was applied for geometry optimizations. In all cases, the nature of the located stationary points was verified through vibrational frequency calculations. The electronic energy was refined by single-point energy calculations at the B3LYP/6–311++G(3df,3pd) (McLean and Chandler, 1980; Krishnan et al., 1980; Clark et al., 1983; Frisch et al., 1984) level. The Gibbs free energies are reported for  $T=298.15$  K. The calculations were performed with the Gaussian programme package (Frisch et al., 2009). In some cases, the Solvation Model Density (SMD) solvent model (Marenich et al., 2009) was applied in order to model the aqueous media.

### 2.2. Pulse radiolysis and steady-state gamma irradiation

Pulse radiolysis was performed with 800 ns pulses of a linear accelerator, and using an optical detection system with a 1 cm cell. Pulse dosimetry was made in air-saturated,  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> KSCN solutions monitored at  $\lambda=480$  nm. A Co-60 gamma facility with 1.8 PBq activity was used for the steady-state gamma irradiation. The dose rate was measured with ethanol–monochlorobenzene (ECB) dosimetry, it was about 5.0 kGy h<sup>-1</sup>.

The radiolysis of water (Reaction (1)) produces hydrated electron ( $e_{aq}^-$ ), hydrogen atom (H<sup>•</sup>) and hydroxyl radical ( $\cdot$ OH) reactive intermediates (the  $G$  values (yields) in parentheses are given in  $\mu$ mol J<sup>-1</sup> units) (Buxton et al., 1988; Spinks and Woods, 1990):



The reactions of  $\cdot$ OH were followed in N<sub>2</sub>O-saturated solution, N<sub>2</sub>O converted the hydrated electrons to hydroxyl radicals (Reaction (2)) (Spinks and Woods, 1990). Reactions of  $e_{aq}^-$  with monuron were investigated in N<sub>2</sub>-saturated solutions containing 5 vol% *tert*-butanol (TBA) to scavenge the hydroxyl radicals (3). When the solution was pre-purged with N<sub>2</sub>, in the absence of TBA, all the three reactive species reacted with the solute. In the presence of dissolved O<sub>2</sub> (in air saturated solutions),  $e_{aq}^-$  and H<sup>•</sup> can react with oxygen ((4) and (5)), and they are converted into superoxide radical/perhydroxyl radical (O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup>) pair. Hence, the attacking species under this condition are  $\cdot$ OH, as well as the O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup> pair ( $\text{p}K_a(\text{O}_2^{\bullet -}/\text{HO}_2^\bullet)=4.8$ ).

In most of experiments  $1 \times 10^{-4}$  mol dm<sup>-3</sup> monuron solutions were investigated. The solutions were saturated with the appropriate gases, N<sub>2</sub>O, N<sub>2</sub>, or air before irradiation.

## 3. Results and discussion

### 3.1. Spectroscopic measurements

In the UV absorption spectrum of monuron there is a well-resolved peak at 245 nm with molar absorption coefficient of 16,350 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, this band is the characteristic  $\pi \rightarrow \pi^*$  excitation band of aromatic ring (Fig. 1). With the increasing dose the intensity of this band decreased and in solutions where the hydroxyl radicals reacted with monuron a new band appeared between 270 and 320 nm, above 1 kGy it disappeared. This band is suggested to belong to the hydroxylated products as it was shown previously on the examples of fenuron (Kovács et al., 2014) and diuron (Kovács et al., 2015). In N<sub>2</sub> saturated solution containing 5 vol% TBA, in which  $e_{aq}^-$  is the main reaction partner (with a little contribution from H<sup>•</sup>) this new band was not observed. In both  $\cdot$ OH and the  $e_{aq}^-$  reactions the absorption band peaking at 245 nm was slightly shifted to shorter wavelengths. This shift may be due to dehalogenation. The  $\lambda_{\text{max}}$  value for the non-halogenated molecule (fenuron) is at 238 nm (molar absorption coefficient: 15377 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). The shift of  $\lambda_{\text{max}}$  to shorter wavelength was the highest in  $e_{aq}^-$  reaction indicating an efficient dehalogenation.

The UV-spectrophotometric measurements show that the degradation is the fastest in air saturated solution, when both  $\cdot$ OH and the O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup> pair may react with monuron. It is the slowest, when only reducing radicals  $e_{aq}^-$  and H<sup>•</sup> are the reaction partners. In the latter case irradiation led to formation of products having low solubility which caused light scattering.

### 3.2. Pulse radiolysis studies

The transient absorption spectrum taken in solution when  $\cdot$ OH reacted with monuron the absorbance in the 300–400 nm range and above 400 nm showed different time dependencies. Above 400 nm the absorbance decayed more slowly than the absorbance at shorter wavelengths. This behaviour showed that during the pulse at least two transient intermediates formed. The one absorbing in the 300–400 nm range may belong to the hydroxycyclohexadienyl radical isomers. In order to check the identification of this peak we repeated these experiments with

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