

Hydroxyl radical induced transformation of phenylurea herbicides: A theoretical study



Viktória Mile^a, Ildikó Harsányi^a, Krisztina Kovács^{a,*}, Tamás Földes^b, Erzsébet Takács^a, László Wojnárovits^a

^a Institute for Energy Security and Environmental Safety, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary

^b Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

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ABSTRACT

Aromatic ring hydroxylation reactions occurring during radiolysis of aqueous solutions are studied on the example of phenylurea herbicides by Density Functional Theory calculations. The effect of the aqueous media is taken into account by using the Solvation Model Based on Density model. Hydroxyl radical adds to the ring because the activation free energies (0.4–47.2 kJ mol⁻¹) are low and also the Gibbs free energies have high negative values ((-27.4) to (-5.9) kJ mol⁻¹). According to the calculations in most of cases the *ortho*- and *para*-addition is preferred in agreement with the experimental results. In these reactions hydroxycyclohexadienyl type radicals form. In a second type reaction, when loss of chlorine atom takes place, OH/Cl substitution occurs without cyclohexadienyl type intermediate.

1. Introduction

Phenylurea herbicides are photosynthesis inhibitors, and are applied to control broadleaf weeds. These herbicides are mostly *N*-dimethyl derivatives bearing various substituents on the aromatic ring. They are highly persistent in the environment with half-lives of several months in the soil. The compounds are regularly detected in surface waters in concentrations up to several μg dm⁻³. Persistent organic pollutants in water matrix may be eliminated by using advanced oxidation processes (AOP). These techniques use aggressive radicals, mainly hydroxyl radicals ([•]OH), to degrade the harmful organic pollutants. The degradation of phenylurea herbicides was investigated by several AOP, e.g. Fenton, photo-Fenton, H₂O₂/UV or by high energy ionizing radiation treatments (Mazellier and Sulzberger, 2001; Canle-Lopez et al., 2005; Bobu et al., 2006; Zhang et al., 2008; Oturan et al., 2010; Kovács et al., 2014, 2015). As it was shown by time resolved pulse radiolysis and pulse photolysis experiments [•]OH reacts with the aromatic ring resulting in hydroxycyclohexadienyl radicals, which transform to stable products hydroxylated in the aromatic ring (phenol type compounds) (Canle-Lopez et al., 2001, 2005; Zhang et al., 2008; Kovács et al., 2014, 2015). [•]OH attack on the methyl groups was found less important than the reaction with the aromatic ring (e.g. Oturan et al., 2010). However, Mazellier and Sulzberger (2001) observed only one product in the heterogeneous photo-Fenton degradation of diuron (3-(3,4-dichlorophenyl)-1-formyl-1-methylurea), which was formed in

the [•]OH attack on a methyl group.

During the complex AOP reactions of the halogen containing phenylureas (e.g. monuron and diuron, Fig. 1) dehalogenation was also observed. In general, dehalogenation is attributed to reductive processes, e.g. in radiolytic reactions to the reactions of hydrated electrons. The most striking result of diuron and monuron investigations is the fact that the dehalogenation is also observed in the reactions of hydroxyl radicals (Tahmassebi et al., 2002; Zhang et al., 2008; Oturan et al., 2010; Kovács et al., 2015, 2016). For example in monuron solution about 40% of [•]OH reactions may induce chloride release (Kovács et al., 2016). The details of these reactions have not been investigated yet.

Two reaction pathways can be visualized: (i) [•]OH addition to the carbon atom when hydroxycyclohexadienyl type radical intermediate is forming, followed by HCl elimination, and (ii) direct [•]OH/Cl⁻ exchange. Tahmassebi et al. (2002) suggested even more complicated mechanisms for the Cl/OH substitution: (i) the dissociation of a C-Cl bond in the pesticide gives a phenylurea radical, which step is followed by an [•]OH addition to this radical, or (ii) a C-Cl reductive cleavage occurs on a previously hydroxylated molecule. Under the usual conditions such two-step reactions should have low probabilities.

The present work focuses on the aromatic ring hydroxylation by applying quantum chemical calculations. The purpose was to clarify the site of attack on the aromatic ring and the mechanism of chlorine elimination. Fenuron (1,1-dimethyl-3-phenylurea), monuron (3-(4-

* Corresponding author.

E-mail address: kovacs.krisztina@energia.mta.hu (K. Kovács).

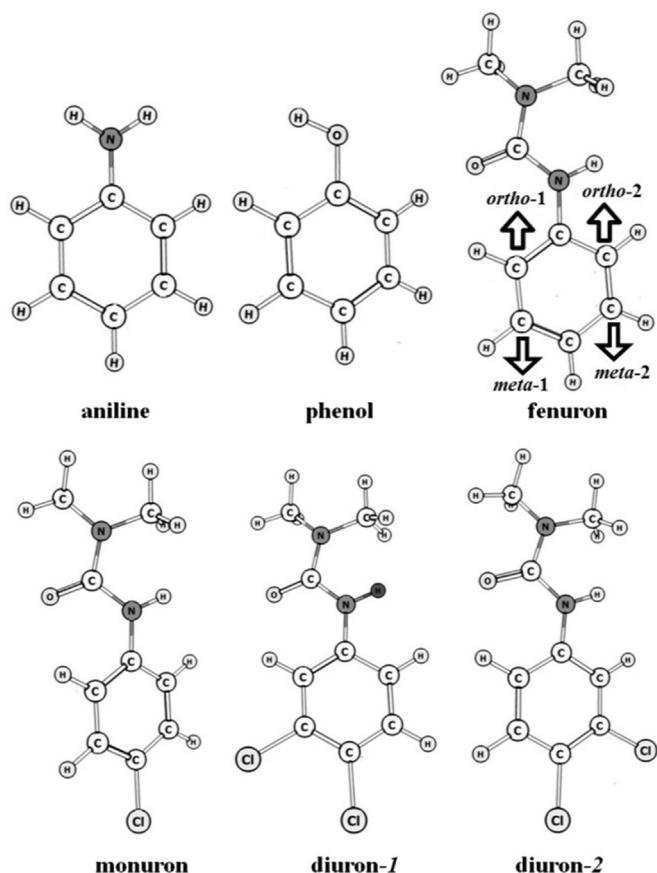


Fig. 1. Structures of the studied molecules: aniline, phenol, fenuron, monuron, diuron-1 and diuron-2. The nomination of the reaction direction (i.e. addition of $\cdot\text{OH}$ to a given carbon atom) is according to the arene substitution pattern. The two *ortho* (*ortho-1* and *ortho-2*) and the two *meta* (*meta-1* and *meta-2*) positions at herbicides are distinguished with 1 and 2 shown in the case of fenuron. The order starting from the phenyl-urea group is the following (counter clockwise): *ipso*, *ortho-1*, *meta-1*, *para*, *meta-2*, *ortho-2*.

chlorophenyl)-1,1-dimethylurea) and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) were chosen from the class of phenylurea herbicides for this study (Fig. 1). Aniline and phenol were also involved as model compounds for the more complicated phenylureas.

The hydroxyl radical reactions with aniline have been previously studied by pulse radiolysis combined with computer optimization procedures. Solar et al., (1986) suggested 54% and 10% $\cdot\text{OH}$ attacks to *ortho*- and *para*-carbon atom, respectively. $\cdot\text{OH}$ radical additions to the aromatic ring of phenol were studied both experimentally (e.g. Albarran and Schuler, 2007) and theoretically (Lundqvist and Eriksson, 2000; Lee et al., 2009; Wu et al., 2012; Jayathilaka and et al., 2014). Catechol and hydroquinone are produced in the catalytic oxidation reaction of phenol (Norena-Franco et al., 2002; Parida et al., 2008). The frequencies of additions to different positions are reported to be: *ipso*: 8%, *ortho*: 50 (2×25)%, *meta*: 8 (2×4)%, *para*: 34% (Albarran and Schuler, 2007). Wu et al. (2012) concluded that the *ortho* adduct is the most stable thermodynamically, followed by the *ipso*, *para* and *meta* ones. According to the charge distribution calculations on phenol the two *ortho* carbon atoms have the highest negative charges (Lundqvist and Eriksson, 2000). The *ipso* and *meta* positions of phenol are not preferred due to a positive charge or a small negative one (Lundqvist and Eriksson, 2000). The results of Wu and co-workers (2012) indicate that the *ortho* addition pathway is dominant, the same result was obtained by Jayathilaka et al. (2014).

Hydroxylated phenylurea herbicides are created during the degradation of pesticides in advanced oxidation processes, e.g. in radiolysis (Kovács et al., 2014, 2015). The directions of the hydroxyl radical addition to the ring are not known from the experiments. The first step

of the degradation has been studied theoretically in cases of diuron by several researchers and all studies agreed that the *ortho* and *para* directions are preferred (Carrier et al., 2009; Ren et al., 2014; Mendoza-Huizar, 2015). However, it is not known yet whether all the reactions have barrier, or some of them proceeds with barrierless mechanism. For the fenuron + hydroxyl radical reaction the detailed calculations of Zeng et al. (2015) suggest hydroxylations in the following order: $C_{ortho-1} > C_{para} > C_{ipso} > C_{meta-1} > C_{meta-2}$ according to the Gibbs free energy of the reaction. In case of activation free energy the order is: $C_{meta-2} > C_{meta-1} > C_{para} \approx C_{ortho-1} > C_{meta-2}$.

2. Methods

The computational analysis was carried out using Density Functional Theory (DFT) methods. Becke's three parameter hybrid functional has been applied with the Lee-Yang-Parr correlation extension, generally known as B3LYP (Becke, 1993). The standard 6-311++G(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. Frequency calculations were also performed for establishing the stationary points (i.e. ground state: frequencies are all positive, transition state: there is one imaginary frequency). The electronic energy was refined by single-point energy calculations at the B3LYP/6-311++G(3df,3pd) level (McLean et al., 1980; Krishnan et al., 1980; Clark et al., 1983; Frisch et al., 1984). The Gibbs free energies are reported for $T=298.15$ K and corrected for $c=1$ mol dm^{-3} . The calculations were performed with the Gaussian program package (Frisch et al., 2009). The Solvation Model Based on Density model (SMD) (Marenich et al., 2009) was applied in order to model the aqueous media. The geometries were also reoptimized under the effect of the solvation model. Based on Gibbs free energies of the reactions and activation free energies we make suggestions for the most probable sites of $\cdot\text{OH}$ attack, and also we clarify the details of the dechlorination reaction.

3. Results and discussion

The dimethylurea-group in the molecule is relatively rigid because of the delocalized electrons. Hence, two possible places of attack for $\cdot\text{OH}$ can be distinguished on the ring at the *ortho* and the *meta*-ring positions. The difference between *ortho-1* and *ortho-2* and between *meta-1* and *meta-2* is the orientation of the C=O group within the dimethylurea moiety. In case of diuron there are two chlorine atoms in the molecule. The possible conformations depend on the direction of C=O group. Diuron-2 is denoted when the *meta* chlorine atom is on the opposite side of C=O group. The names and the possible reaction pathways for the sake of clarity are shown in Fig. 1. The optimized bond length values are provided in Supplementary Material (Table 1S). The bond lengths are in good agreement with results of former calculations (Ren et al., 2014; Mendoza-Huizar, 2015). The typical $C_{\text{ring}}-C_{\text{ring}}$, $C_{\text{ring}}-\text{H}$ and $C_{\text{ring}}-\text{N}$ next to the ring and $C_{\text{ring}}-\text{Cl}$ bond lengths are 1.39, 1.08, 1.41 and 1.76 Å, respectively.

Table 1 contains the values of the Gibbs free energies (ΔG) and the activation free energies (ΔG^\ddagger) relative to the reactants. All modelled reactions are found to be exergonic. Calculations suggest larger stabilization in the case of chlorine substituted aromatic rings (monuron: *para*; diuron-1: *meta-1*, *para*; diuron-2: *meta-2*, *para*). $\cdot\text{OH}$ attacks at the *para*-positions are energetically the most favorable reactions for the phenylureas. Based on the calculated Gibbs free energy and activation free energy data the *ortho* and *para* reactions take place with almost equal probability for aniline, while the *ipso* and the *meta*-reactions are energetically less favorable as it was suggested by Solar et al. (1986) based on pulse and gamma-radiolysis experiments. Similarly to aniline for phenol the *ortho* and *para* reactions are energetically favored, however, because of the low Gibbs free energy

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