

## Hydroxyl Radical Reaction with Monuron

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### Abstract

On the example of monuron, aromatic ring hydroxylation reactions were studied by Density Functional Theory calculations. In order to model the aqueous media the Solvation Model Density technique was used. Based on the relatively low activation energies of hydroxyl radical additions to *ipso*-, *ortho*- and *meta*-positions of the benzene ring (19-42 kJ mol<sup>-1</sup>) and also the Gibbs free energies ((-16)-(-41) kJ mol<sup>-1</sup>) of reactions, hydroxyl radical addition to any of these positions may take place. However, according to the calculations the *ortho*-addition is preferred in agreement with the experimental results. In these reactions hydroxycyclohexadienyl type radicals form. The first step in the mechanism of *para*-reaction is OH/Cl substitution without cyclohexadienyl type intermediate. The results of theoretical calculations here are also in agreement with the experimental results which show that the hydroxyl radical reaction with monuron in 40% results in Cl elimination.

### Introduction

In Advanced Oxidation Processes hydroxyl radicals are the reactive intermediates which induce the decomposition of toxic organic compounds present in water matrices. Previously, the degradation of monuron (3-(4-chlorophenyl)-1,1-dimethylurea) herbicide in dilute aqueous solution (1×10<sup>-4</sup> mol/dm<sup>3</sup>) was studied in our laboratory. Based on the experimental results, the main process is the reaction between monuron and •OH forming hydroxycyclohexadienyl radical.

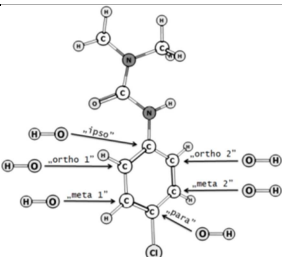
### Experimental

The calculations were performed by using Density Functional Theory (DFT) [1]. Becke's three parameter hybrid functional was used with the Lee-Yang-Parr correlation one, generally known as B3LYP [2] The standard 6-311G++(d,p) [3-4] basis set was applied for optimizing the structure, which contains diffuse [5] and polarization [6] functions to improve the description of the hydrogen bonds because of presence of urea-group. In order to model the aqueous media we applied the Solvation Model Density (SMD) technique [7]. First, the optimized geometry of the isolated compounds was determined, then the complexes were put together manually from the two optimized geometries. To determine the structures of the transition state and the product, the bond length between C (given position) and •OH was changed in equidistant steps and at each point a constrained geometry optimization was carried out. The structure at the maximum of the energy curve is probably very close to the real transition state and the geometry at energies minima correspond to addition complex. In all cases, the nature of the extrema was verified through frequency calculations. The electronic energy was refined by single-point energy calculations at the B3LYP/6-

311++G(3df,3pd) level [3-4]. All energies are reported at 298.25 K. The calculations were performed with the Gaussian program package [8].

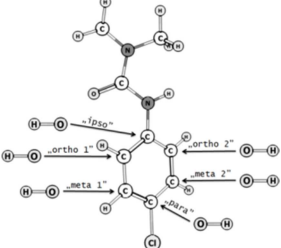
## Results and discussion

The Gibbs energies of the reactions ( $\Delta_r G$ ) and activation energies ( $E_a$ ) of the aromatic ring hydroxylation are collected in Table 1 and Table 2. The data in Table 1 were obtained without water model (i.e. gas phase) and Table 2 shows the data with using SMD water model. Both using water model and without the applied water model  $\Delta_r G$  is significantly different in case of *para*-reaction than in the other reactions. The *meta* addition path is energetically less favourable than the *ipso*- and the *ortho1*- and the *ortho2*-hydroxylation due to the effect of electron donating groups. The Gibbs free energies of the reactions are somewhat higher in presence of water except for *para* reaction where the energy is lower due to solvation energy of chlorine.

Possible positions of attack.	Position	$\Delta_r G / \text{kJmol}^{-1}$	$E_a / \text{kJmol}^{-1}$	$d_1 / \text{\AA}$	$d_2 / \text{\AA}$
	<i>ipso</i>	-30.15	42.27	2.006	1.417
	<i>ortho 1</i>	-35.46	31.51	2.002	1.436
	<i>ortho 2</i>	-40.32	16.06	2.117	1.456
	<i>meta 1</i>	-19.21	38.76	2.000	1.445
	<i>meta 2</i>	-20.78	32.05	2.024	1.448
	<i>para</i>	-155.91	39.49	2.069	1.259

**Table 1.** Thermodynamic and structural properties of hydroxyl radical reactions with the aromatic ring of monuron at 298.25 K in gas phase (without applied water model):  $\Delta_r G$  Gibbs free energy,  $E_a$  activation energy,  $d_1$  and  $d_2$  C-•O distances in the transition state and in the product, respectively.

Activation energies without using water model are between 30-42  $\text{kJ mol}^{-1}$  except for *ortho2* reaction, where the activation energy of hydroxylation is significantly lower. In aqueous media  $E_a$ 's are somewhat lower (20-30  $\text{kJ mol}^{-1}$ ). In the applied SMD at the transition state of *ortho 2* has not been found yet. Further calculations are in progress in order to find the TS or prove this reaction is barrierless.

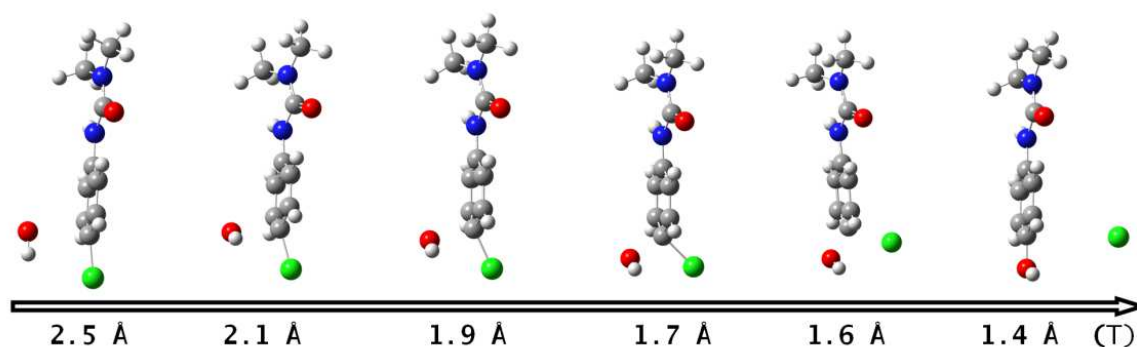
Possible positions of attack.	Position	$\Delta_r G / \text{kJmol}^{-1}$	$E_a / \text{kJmol}^{-1}$	$d_1 / \text{\AA}$	$d_2 / \text{\AA}$
	<i>ipso</i>	in progress	29.70	2.025	in progress
	<i>ortho 1</i>	-30.31	19.55	2.076	1.457
	<i>ortho 2</i>	-36.53	in progress		1.462
	<i>meta 1</i>	-18.93	30.03	2.076	1.461
	<i>meta 2</i>	-16.10	29.92	2.118	1.462
	<i>para</i>	-179.64	27.59	2.152	1.318

**Table 2.** Thermodynamic and structural properties of hydroxyl radical reactions with the aromatic ring of monuron at 298.25 K in aqueous media (using SMD water model):  $\Delta_r G$

Gibbs free energy,  $E_a$  activation energy,  $d_1$  and  $d_2$  C-•O distances in the transition state and in the product, respectively.

The distance of  $C_{\text{ring}}-\text{O}_{\text{radical}}$  of transition state of *ortho*2-hydroxycyclohexadienyl radical differs from the other cases in gas phase. This process has lower activation energy. In the products of *ortho*1-cases the  $C_{\text{ring}}-\text{O}_{\text{radical}}$  lengths are somewhat shorter because of developed hydrogen bond both in water and in gas phase. The effect of hydrogen bond in TS can be observed just in *ipso*-reaction in aqueous medium. The C-•O bond lengths in cyclohexadienyl radicals and in their TS are shorter in gas phase than in aqueous medium.

In the *para*-case, the reason of the different value of  $\Delta_r G$ , is the changer of reaction mechanism from radical addition to dechlorination reaction. It is worth to mention that the bond lengths of  $C_{\text{ring}}-\text{O}_{\text{radical}}$  of end product of *para* reaction are significantly different. Without using water model the end product is phenoxy type radical, i.e. the released chlorine atom tear down the hydrogen atom from the •OH radical. In the applied water model (after the Cl/OH substitution) the hydroxylated molecule is stabilized by solvation. The attack of the •OH radical to *para*-position is shown in Figure 1. Experiments suggest that the phenoxy radicals are created during the attack of the •OH radical in aqueous medium. In order to better understand the exact mechanism further calculations are necessary paying special attention to the effects of water.



**Figure 1.** Conformational changes during hydroxyl radical reaction in *para* case. In the lower part of the figure the  $C_{\text{ring}}-\text{O}_{\text{radical}}$  distances are shown in Å units.

## Conclusion

The aromatic ring hydroxylations were studied by quantum chemical calculations. In the *ipso*-, *ortho*- and *meta*-reaction simple addition with cyclohexadienyl type radical formation takes place. In case of *para* hydroxylation reaction OH/Cl substitution occurs without cyclohexadienyl type intermediate. Solvation plays a very important role in determining the directions of reactions.

## Acknowledgements

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