

Theoretical and Experimental Approach for the Study of 2,4-Dichlorophenoxyacetic acid Photodegradation: C–O versus C–Cl Bond Dissociation Energies in the Gas Phase and Aqueous Medium

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RECEIVED APRIL 13, 2009; REVISED SEPTEMBER 17, 2009; ACCEPTED NOVEMBER 2, 2009

Abstract. A theoretical, gradient-corrected Hartree-Fock-density functional theory (HF-DFT) approach was applied to the determination of the bond dissociation energy (BDE) for the photodegradation processes of the 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide in the gas phase and in aqueous medium. According to the results of these calculations, the phenoxy C–O homolytic BDE value was found to be approximately two times lower than the corresponding C–Cl (2) and C–Cl (4) BDE ones, in both gas phase and under continuous solvation by water. An experimental study of the 2,4-D photodegradation reaction kinetics and photoproducts was also performed in water. At lower concentration, the formation of only two photoproducts (2-Cl- and 4-Cl-phenoxyacetic acid) was observed, whereas at higher concentration, three photoproducts were formed, with 2,4-dichlorophenol as the third one. These photoproducts appeared competitively within about 40–80 min, and were eventually photodecomposed. The experimental data are in good agreement with the results of our HF-DFT calculations.

Keywords: 2,4-D herbicide; photodegradation; Hartree-Fock-density functional theory (HF-DFT) approach; bond dissociation energy processes

INTRODUCTION

Chlorophenoxy acids are widely used as herbicides in agriculture. Because of their relative stability and photostability in natural waters, they are considered as persistent organic pollutants (POP), and they constitute a serious environmental problem. In the last decade, the photodegradation reactions and other physicochemical processes of chlorophenoxy acids, especially 2,4-dichlorophenoxyacetic acid (2,4-D), occurring in the environment have been investigated by several computational and experimental methods in various aqueous media.^{1–7} For example, the photocatalytic degradation of these herbicides has been investigated in agricultural used waters,¹ whereas the efficiency of three different photochemical systems, including direct photolysis (UV

irradiation at 254 nm), assisted photochemistry (UV irradiation + H₂O₂) and photo-Fenton reaction (UV irradiation + H₂O₂ + Fe^{III}), has been compared for the photodegradation of some chlorophenoxy acids in aqueous solution at room temperature.² Also, the photodegradation of 2,4-D has been investigated in various iron-mediated oxidation aqueous systems³. The TiO₂-photocatalyzed oxidation of 2,4-D and three other chlorophenoxyacetic acids has been studied by Watanabe *et al.*⁴ in UV irradiated aqueous TiO₂ dispersions to obtain mechanistic details, the initial mechanistic sequences being theoretically predicted by molecular orbital (MO) calculations of frontier electron densities and point charges of all the atoms in these chlorophenoxyacetic acids. Also, Peller *et al.*⁵ have combined computational (quantum chemical) and experimental methods to eluci-

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date the reactivity of the hydroxyl radical in the degradation of 2,4-D, measured from γ -radiolysis experiments with both ^{18}O -labeled and unlabeled water. These authors have calculated the reaction energies of radical intermediates formed from various hydroxyl radical attacks on 2,4-D, and have found that the kinetically-controlled $\cdot\text{OH}$ attack *ipso* to the ether functionality was the main reaction pathway, and was followed by homolytic elimination of the ether side chain.⁵ Recently, we have undertaken an experimental study of the photodegradation kinetics and of the toxicity of 2,4-D in water, and we have carried out preliminary theoretical calculations.⁶ In another recent investigation, Tunega *et al.*⁷ have presented the hydrogen-bonded adsorption processes of several chlorophenoxy acid derivatives with soil, and they have described the possibilities for accurate quantum chemical calculations of these processes. The authors attempted to include the solvent effect in three different ways: by the explicit inclusion of water molecules, by the use of a continuum solvation model, and by the combination of these two models.

The existence of complex photodegradation mechanisms in aqueous media, involving the role of $\cdot\text{OH}$ radicals in the direct and/or indirect photolysis, has been postulated for chlorophenoxy acids, but the knowledge of the mechanistic pathways still remains incomplete.⁴⁻⁶ Because of the presence in the environment of chlorophenoxy acids at the trace level and of the formation of possibly toxic metabolites, it is very important to propose a detailed model of these mechanisms, and to perform theoretical calculations to determine the stability and photochemical reactivity of chlorophenoxy acids.

Therefore the main goal of this work is to develop an *ab initio* Hartree-Fock-density functional theory (HF-DFT) approach, and to apply it to the stability and photoreactivity of 2,4-D both in the gas phase and in water. On the other hand, our experimental data on the 2,4-D photodegradation kinetics and photoproduct identification will also permit to corroborate this theoretical approach.

RESULTS AND DISCUSSION

Experimental observations

We have shown experimentally that the photodegradation reaction of 2,4-D follows first-order kinetics in de-ionized and natural river water at room temperature, when the solutions were submitted to UV irradiation by a photolysis lamp. The 2,4-D photodegradation half-lifetimes ($t_{1/2}$) and apparent 1st order rate constants (k_1) were evaluated by analyzing our experimental data obtained at relatively small 2,4-D concentrations (10–100 $\mu\text{mol L}^{-1}$). As can be seen in Table 1, the $t_{1/2}$ values are relatively short (less than 30 min), which shows that the photodegradation of 2,4-D is rather rapid in aqueous

Table 1. Experimental kinetic data for the photodegradation of 2,4-D in aqueous media^(a)

Medium	$t_{1/2}$ / min	k_1 / min^{-1}
De-ionized water	22.5 (\pm 2.5)	0.031
Natural river water	28.0 (\pm 3.0)	0.025

^(a) Concentration of 2,4-D = 80 $\mu\text{mol L}^{-1}$.

media. Using a different photochemical reactor, Fdil *et al.*² previously found a similar kinetic behavior for the 2,4-D photodegradation in de-ionized water. Moreover, the $t_{1/2}$ and k_1 values are very close in both aqueous media under study (Table 1), which indicates that the 2,4-D photodegradation rate is not significantly influenced by the presence of impurities in natural river water.

On the contrary, in the absence of UV irradiation, 2,4-D was found to be extremely stable in aqueous solutions. Indeed, no spontaneous degradation of this compound was noticed in these aqueous media during periods of several weeks.

In order to elucidate the possible pathways of photodegradation of 2,4-D in aqueous medium, an attempt was made to identify the photoproducts by means of HPLC. Two photoproducts were formed at solute lower concentration (about 80 $\mu\text{mol L}^{-1}$) and three photoproducts at higher concentration (about 800 $\mu\text{mol L}^{-1}$). The formation of these three photoproducts took place competitively within about 40–80 min, followed by their photodecomposition. Upon comparison with the retention time values of the standard compounds, the respective HPLC retention time values of these photoproducts indicated the formation of 2-Cl-phenoxyacetic acid and 4-Cl-phenoxyacetic acid at 2,4-D lower concentration, and of 2-Cl-phenoxyacetic acid, 4-Cl-phenoxyacetic acid and 2,4-dichlorophenol at 2,4-D higher concentration.

In the following section, the results of quantum chemical calculations, are compared with these experimental data obtained for 2,4-D photodegradation in aqueous media.

Theoretical results and implications arising thereof

We have carried out a complete, quantum chemical study of the title system which has allowed us to verify whether our theoretical calculations, based on a thermodynamic analysis of the bond dissociation processes, were in agreement with the above-described experimental study of the 2,4-D photodegradation products, and the relative importance of the various, photodissociation pathways.

Therefore, based on a HF-DFT approach we have calculated by the B3-LYP^{8,9} and the PBE1-PBE¹⁰ methods the bond dissociation reaction energies and enthalpies (BDE) of the dissociation asymptotes corresponding to the bond cleavage processes in both gas

Table 2. Computed thermochemical parameters characterizing the 2,4-D homolytic bond dissociation processes in gas phase

Bond	B3LYP			PBE1-PBE		
	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$
C–Cl(2)	366.6	367.0	369.5	386.9	387.4	389.9
C–Cl(4)	370.0	370.4	372.9	389.4	389.8	392.3
(C ₆ H ₃ Cl ₂)O–C	187.5	187.3	189.8	210.2	210.2	212.7

Table 3. Computed thermochemical parameters characterizing the 2,4-D homolytic bond dissociation processes in water treated as a continuous solvation medium

Bond	B3LYP			PBE1-PBE		
	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$
C–Cl(2)	366.7	367.1	369.6	386.8	387.3	389.8
C–Cl(4)	370.3	370.7	373.2	389.4	389.8	392.3
(C ₆ H ₃ Cl ₂)O–C	179.4	179.1	181.6	201.8	201.8	204.3

Table 4. Computed thermochemical parameters characterizing the homolytic OH bond dissociation process of water in gas phase and in aqueous environment

Bond	B3LYP			PBE1-PBE		
	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_0}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{298.15}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{298.15}}{\text{kJ mol}^{-1}}$
O–H						
Gas-phase	473.9	476.4	478.8	468.9	471.4	473.9
Solvated	474.8	477.3	479.8	470.4	472.9	475.4
Exp. 11.	-	-	492.0	-	-	492.0

phase and in water, the later medium being treated as a continuous dielectric with a relative dielectric constant $\epsilon = 78.39$ (see for details in Experimental Section). The calculated thermochemical parameters, including the ΔE_0 , $\Delta E_{298.15}$ and $\Delta H_{298.15}$ values for the 2,4-D homolytic bond dissociation processes in both gas phase and water, are given in Tables 2 and 3. As can be seen, a good agreement was found between the BDE values obtained by both methods.

For comparison purposes, we have also determined by means of the same methods the O–H BDE (ΔE_0 , $\Delta E_{298.15}$ and $\Delta H_{298.15}$) values of a H₂O molecule in gas phase and in a medium continuously solvated by bulk water. Indeed, the dissociation asymptote corresponding to the H₂O dissociation pathway is, beyond any doubt, a competitive one to those already mentioned for 2,4-D photodegradation, due to the reasons outlined further in the paper. These results are summarized in Table 4. As can be seen, the calculated thermochemical parameter values presented in Table 4 are in excellent agreement with the most accurate experimental data for these quantities.¹¹ In a sense, this agreement validates the applicability of the computational methodology used

for the purpose of the present study.

Optimized geometries of all the relevant species involved in the mentioned dissociation pathways of 2,4-D in gas phase are shown in Figure 1, using the atomic numbering indicated for 2,4-D in Figure 2. The relevant geometry parameters have been calculated for 2,4-D and the radical species arising from the dissociation pathways under study, which correspond to the minimums on the B3-LYP and PBE1-PBE/6-31++G(d,p) PESs in gas phase and in water environment. These data are available from the authors upon request.

Regarding the central point of the present study, the thermochemistry of bond dissociation processes, the homolytic BDE of the C–O bond is about two times lower than the C–Cl(2,4) BDEs ones, as can be seen from Tables 2 and 3. This important result indicates that, thermodynamically, the C–O bond should be preferably dissociated rather than the C–Cl ones. The continuous solvation by water notably influences only the C–O BDE, the C–Cl ones being affected only very slightly by this, basically electrostatic, stimulation of the solvating medium. However, even in the case of the C–O BDE, the induced relative changes it experiences

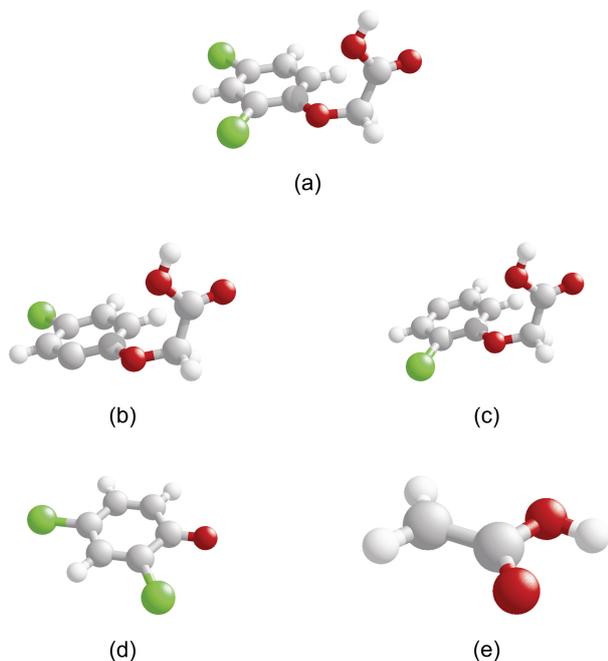


Figure 1. Geometries corresponding to the minima on B3LYP/6-31++G(d,p) PESs of 2,4-dichlorophenoxyacetic acid (a) and of the radical species (b)–(e) arising from various dissociation asymptotes considered in the present study.

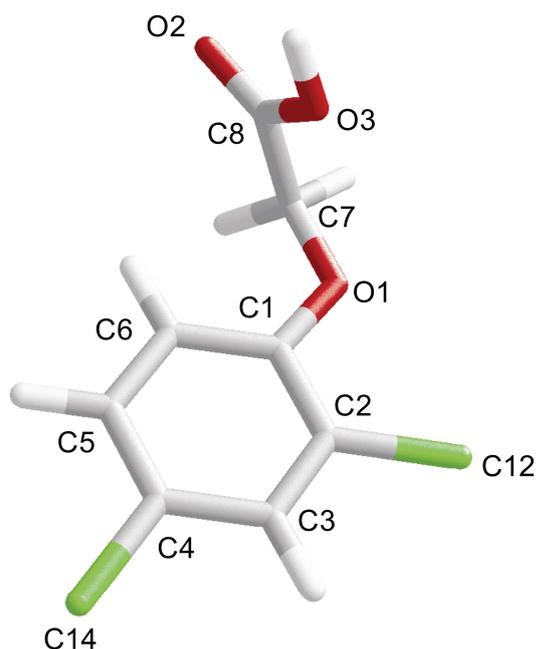


Figure 2. Atomic numbering scheme for 2,4-dichlorophenoxyacetic acid.

upon solvation are still less than 5 %. It is interesting to note that the calculated O–H BDE value is even larger, *i.e.* approximately 100 kJ mol^{-1} , than the C–Cl BDEs. This particular O–H BDE value is somewhat more affected by continuous solvation than the C–Cl ones, but in a lesser extent than the C–O one.

These theoretical, thermochemical parameters imply the following interpretation for the occurrence of the photodegradation mechanism of 2,4-D in an aqueous medium. First of all, the previously outlined purely thermodynamical arguments would favor the C–O dissociation asymptote over the C–Cl (*i*) ones. This preferential dissociation of the phenoxy C–O bond compared to the C–Cl one in 2,4-D is also supported by the experimental results of Choudry and Hutzinger,¹² who found that the breaking of the ether C–O bond was also favored relative to the C–Cl bond in the photochemical degradation of some chlorinated dibenzo-*p*-dioxines. Moreover, both of the 2,4-D C–O and C–Cl asymptotes would be expected to be preferred over the HO–H bond dissociation of the water molecule, as can be seen by comparing the C–Cl (2,4) and C–O bond homolytic dissociation thermochemical parameter values with those of the O–H bond homolytic dissociation process (Table 4). However, secondly, due to the much larger concentration of water acting as a solvent, the production of $\cdot\text{OH}$ radicals upon UV illumination of the system is by far the most predominant process occurring in aqueous solution. Because of the high reactivity of the $\cdot\text{OH}$ radical species, the 2,4-D molecules are frequently attacked by those species. Resulting from their relatively large size, the chlorine atoms of 2,4-D molecules would be much more exposed to such attacks. As a consequence, when the solute (2,4-D) initial concentration is relatively small, the predominating photodegradation products are those corresponding to the C–Cl (*i*) dissociation asymptotes. Experimental observation of the formation of only 2-chlorophenoxyacetic acid and 4-chlorophenoxyacetic acid as photolytic products at low initial concentrations of 2,4-D in an aqueous medium may thus be attributed to basically kinetic effects, which are manifestly due to purely steric reasons. Only when the solute initial concentration becomes higher, the thermochemistry comes into play and the species arising from photolysis along the C–O asymptote (*i.e.* 2,4-dichlorophenol) becomes observable among the formed photodegradation products. If the C–O BDE values were higher than the C–Cl ones, most probably this photodissociation product would not be observed even at relatively high solute concentrations.

However, the theoretical thermochemical analyses presented in this study strongly suggest that, in the gas phase and in conditions of very low humidity, the formation of C–O photolytic products would be very probably favored.

EXPERIMENTAL SECTION

Materials and experimental procedures

2,4-D and 2-chlorophenoxyacetic acid were obtained from Acros. 4-chlorophenoxyacetic acid was purchased

from Riedel-de-Haën, and 2,4-dichlorophenol from Aldrich. Acetonitrile and acetic acid of analytical grade were supplied by Prolabo. De-ionized water was utilized for the preparation of solutions.

The kinetics of photodegradation of 2,4-D ($10\text{--}800\ \mu\text{mol L}^{-1}$) was investigated in de-ionized water and in natural river water samples (collected in Seine) at room temperature during 40–80 min. Photochemical experiments were performed under UV irradiation, using a HBO Osram 200 W high pressure Hg lamp located at 45 cm from the photo-reactor, a Hellma standard quartz cell ($1\ \text{cm}^2$ section; volume = 3 mL) which was fixed on an optical bench. Kinetics were monitored by high-performance liquid chromatography (HPLC) analysis with UV absorption detection, and the identification of pesticides and their photoproducts was based on the comparison of the HPLC retention time (t_r) values in the irradiated solutions with those of the authentic compounds, using the same HPLC conditions as those previously described.¹³

Computational methods for the theoretical approach

To locate the stationary points on the investigated potential energy hyper-surfaces (PESs) of the species relevant to the various photochemical degradation pathways of 2,4-D in gas phase and aqueous environment, full geometry optimizations thereof were carried out in both gas-phase and in solution, using the Schlegel's gradient optimisation algorithm.¹⁴ Subsequently, after locating the stationary points on the PESs under study, their character was tested by computing the harmonic vibrational frequencies. The absence of imaginary frequencies (*i.e.*, negative eigenvalues of the second-derivative matrix) was used as a criterion that a particular point on the PES corresponded to a minimum-energy structure (instead of, *e.g.*, being a saddle point).

The influence of the solvent on the energetics of bond dissociation processes for the species under study was accounted for in the framework of the self-consistent reaction field (SCRF) methodology, employing the Onsager's cavity model.^{15–18} Within this approach, the solute species are placed in a suitably chosen spherical cavity with a radius a_0 and are surrounded by the solvent, and treated as a uniform dielectric continuum with a dielectric constant ϵ . The cavity radius a_0 is estimated for each system by a gas-phase calculation of molecular volume for the minimum on the gas-phase PES employing Monte-Carlo integration techniques, prior to the geometry optimizations and frequency calculations within the solvent. The electrostatic field (E_R) produced by the reaction of the solvent on the solute dipole moment was calculated by means of the Onsager model:

$$E_R = -g\mu' \quad (1)$$

where μ' denotes a modified dipole moment, suitably scaled in order to set the center of cavity to the center of electronic distribution for the ionic species. The proportionality constant g depends on the cavity radius and the dielectric constant:

$$g = \frac{2 \cdot (\epsilon - 1)}{(2\epsilon + 1) \cdot a_0^3} \quad (2)$$

The geometries of the species under study were optimized using two hybrid Hartree-Fock (HF) – density functional theory (DFT) based methodologies. The first methodology is based on the combination of the Becke's three-parameter adiabatic connection exchange functional (B3)⁸ with the Lee-Yang-Parr (LYP)⁹ correlation functional (B3-LYP method). The second DFT methodology, based on PBE1 exchange functional combined with the PBE correlation one¹⁰ (PBE1-PBE method) is characterized by certain further improvements over the other DFT functional methods. Indeed, generally the later methods are constructed with the main aim of improving the well-known deficiency in their long-range behavior. For example, the DFT functional method mPW1PW91¹⁹ provides an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling as well as a smoother potential. Both of the employed computational methodologies can be considered as hybrid HF-DFT (*i.e.* they include an admixture of HF exchange energy), in contrast to the "pure" DFT ones.

The standard Pople-type 6-31++G(d,p) basis set was employed for orbital expansion, solving the Kohn-Sham (KS) SCF equations iteratively for each particular purpose of this study, along with the "fine" (75, 302) grid for numerical integration (75 radial and 302 angular integration points) in all DFT calculations.

Thermochemistry of the homolytic bond dissociation processes was analyzed in the following way. The energies for each of the involved species, corresponding to the minima on the explored PESs at $T \rightarrow 0$ K were corrected by the zero-point vibrational energies, computed on the basis of harmonic vibrational analysis. Subsequently, the rotational, vibrational and translational contributions were added to the obtained $E(0)$ values, in order to get the $E(T)$ ones (for $T = 298.15$ K). All of these contributions were calculated on the basis of standard statistical-mechanics expressions for an ideal gas constituted of harmonic oscillators within a canonical ensemble.²⁰ The corresponding enthalpies $H(T)$ were calculated from equation (3):

$$H(T) = E(T) + RT \quad (3)$$

Finally, the homolytic bond dissociation reaction energies ($\Delta_r E^\circ$) and enthalpies ($\Delta_r H^\circ$) were calculated

from the standard expressions for the two corresponding quantities, given in equations (4) and (5):

$$\Delta_r E^\circ = \sum_p E_p - \sum_r E_r \quad (4)$$

$$\Delta_r H^\circ = \sum_p H_p - \sum_r H_r \quad (5)$$

where the indices “*p*” and “*r*” represent, respectively, the reactants and the products of the processes under study.

All quantum chemical calculations for the purpose of the present study were carried out with the Gaussian 03 series of codes.²¹

CONCLUSIONS

We have demonstrated in this work that an *ab initio* and density functional theory (DFT) approach, based on the B3-LYP and PBE1-PBE quantum chemical methods, allows one to calculate that the homolytic BDE of the C–O bond is about two times lower than the C–Cl (2,4) BDEs, for the dissociation processes of 2,4-D in the gas phase and in aqueous medium. Under these conditions, it can be theoretically predicted that, thermodynamically, the 2,4-D C–O bond should be preferably dissociated over the C–Cl ones. It is interesting to emphasize that these theoretical thermodynamic calculations are well corroborated by our experimental results on the photodegradation reaction of the 2,4-dichlorophenoxy acid herbicide in aqueous medium.

Acknowledgements. This work was financially supported in part by the French Ministry of Foreign Affairs and the Macedonian Ministry of Education and Sciences (PAI INTEGRAFM Project N°08216RJ, 2004-2005).

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SAŽETAK

Teorijski i eksperimentalni pristup za studiju 2,4-diklorofenoksiacetne kiseline fotodegradacijom: C–O *versus* C–Cl energije disocijacije veza u plinskoj fazi i vodenom mediju

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Teorijski, gradijentno-korigiran pristup baziran na Hartree-Fock teoriji funkcije gustoće (engl. *Hartree-Fock-density functional theory* (HF-DFT)) je upotrijebljen za određivanje energije disocijacije veze (engl. *bond dissociation energy* (BDE)) za procese 2,4-diklorofenoksiacetne kiseline (2,4-D) herbicida u plinskoj fazi i u vodenom mediju. Prema rezultatima ovih izračuna, homolitička BDE vrijednost fenoksi C–O veze je nađena da je otprilike dva puta manja od odgovarajuće onih BDE vrijednosti za C–Cl (2) i C–Cl (4), i u plinskoj fazi i pod stalnom hidratacijom. Eksperimentalno istraživanje 2,4-D kinetike fotodegradacijske reakcije i fotoprodukata se također odvijalo u vodi. Pri nižim koncentracijama, uočeno je nastajanje samo dva fotoprodukta (2-Cl i 4-Cl-fenoksiacetna kiselina), dok pri višim koncentracijama, nastaju tri fotoprodukta, (prethodna dva) s 2,4-diklorofenol kao trećim. Ovi fotoprodutki su nastajali kompetitivno unutar oko 40–80 min, i na kraju su se fotorazgradili. Eksperimentalni podaci su u dobrom slaganju s rezultatima naših HF-DFT izračuna.