

On the Degradation Pathway of Glyphosate and Glycine

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Abstract: Glyphosate is a systemic and non-selective herbicide consisting of a glycine and a phosphonomethyl group [1]. The use of glyphosate-based herbicides (GBHs) has increased significantly as to be worthy of attention in the health areas, both environmental and human health [2]. In case of treatment, e.g. water depollution, it is important to know the details of molecular degradation mechanism. Computation models open the possibility of studying such process in silico. In processes that occur in liquid phase solvent plays an important rule. One alternative to include solvent effects in quantum chemical calculations is the solvent implicit model. There are several models and they have proved to be very useful to take into account macroscopic effects but they are poor in describing microscopic detail, such as bond-breaking process. Another alternative is to include solvent explicitly, by means of addition of solvent molecules, i.e. microsolvation. We studied the degradation mechanism of glyphosate and glycine, sketched in Scheme 1. All calculations were performed using the GAUSSIAN 09 package [3]. We performed geometry optimizations and intrinsic coordinate reaction (IRC) [4] calculation using aug-cc-pVDZ basis set [5] and M062X [6] functional. Solvent effects were included by means of both microsolvation and the polarizable continuum solvation model IEF-PCM [7]. We found two degradation pathways of glycine and glyphosate. Both routes lead to a decarboxylation of the molecule. In the case of glyphosate the product formed was the aminomethylphosphonic acid (AMPA), which is one of the degradation product already reported [4].



Concerted Mechanism





Scheme 1 – Glycine (R = H) and Glyphosate ($R = PO_3H_2CH_2$) degradation mechanisms: concerted (up) and stepwise (down) mechanisms

The energy barrier is quite similar for both molecule, 3.24 eV and 3.13 in the concerted mechanism for glycine and glyphosate, respectively, and 1.90 eV and 1.36 for glycine and 1.90 eV and 1.09 eV for glyphosate in the two-step mechanism for IEF-PCM. The



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concerted mechanism is characterized by a proton transfer, from nitrogen to carbon vicinal atom, accomplish by the breaking of the C—C bond. The stepwise mechanism, which occurs in two steps, begins with decarboxylation followed by the proton transfer. When explicit water molecules are included, mechanism profiles still the same but energy barriers not. Transition states were characterized to each system, with explicit water molecules or not. Water molecules were included in order to preserve the transition state of that obtained with only implicit solvent. Although transition states differ, degradation mechanism is essentially the same. Concerted mechanism seems to be assisted by water molecules, which take a part in the proton transference process. This assistance reduces the energy barrier considerably, as shown in Figure 1. In glycine case energy barrier is reduced by almost half when two water molecules are included.



Figure 1 – Glycine IRC pathways: (a) concerted and stepwise mechanisms in implicit solvent model; (b) concerted mechanism with (dashed line – right Y axis) and without (solid line – left Y axis) explicit water molecules (isolated water molecule total energy is -76.41522075 hartree).

In summary, two mechanisms were presented to the degradation of glycine and glyphosate molecule. Although both routes are globally energetic equivalent, the stepwise mechanism needs lower activation energy and might be the most common chemical degradation pathway.

Key-words: Glyphosate, Glycine, Degradation Pathway, Microsolvation

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