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GLOBAL AND LOCAL REACTIVITY DESCRIPTORS FOR PICLORAM HERBICIDE: A THEORETICAL QUANTUM STUDY

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In this work, we studied the reactivity of picloram in the aqueous phase at the B3LYP/6-311++G(2d,2p) and MP2/6-311++G(2d,2p) levels of theory through global and local reactivity descriptors. The results obtained at the MP2 level indicate that the cationic form of picloram exhibits the highest hardness while the anionic form is the most nucleophilic. From the Fukui function values, the most reactive site for electrophilic and free radical attacks are on the nitrogen in the pyridine ring. The more reactive sites for nucleophilic attacks are located on the nitrogen atom of the amide group and on the carbon atoms located at positions 2 and 3 in the pyridine ring.

Keywords: picloram; reactivity; Fukui.

INTRODUCTION

Picloram (4-amino-3,5,6-trichloro-2-pyridincarboxylic acid) is a herbicide useful for broadleaf weed control in pasture and rangeland, wheat, barley, oats, and for woody plant species.[1] Also, picloram is recognized as the most persistent herbicide of the chlorobenzoic acid family in the soil environment.[2,3] However, despite its persistence in soils, picloram has been detected in surface water and groundwater.[4] This fact has done that picloram is being considered as a potential groundwater contaminant.[5] It is important to mention that human exposure to higher levels of picloram herbicide can cause damages to the central nervous system, loss of weight, diarrhea and weakness.[6] Considering these facts, it is not so strange that the efforts of many researchers have been focused in developing new and efficient remediation treatments to clean picloram from groundwater.[6-10] Reports in the literature indicate that picloram is susceptible to fast photodegradation in soils, with a half-life of 2.6 days.[6] However, an induced chemical degradation of picloram is slow with a half-life ranging of 9 to 16 years.[7] Additionally, picloram has been removed from water through adsorption,[8-12] heterogeneous photocatalysis,[13,14] zero-valent metals,[15,16] electrochemical advanced oxidation[17] and microbial degradation[18-23] processes. In most of the cases, picloram degradation has been found slow and incomplete.[5,19-27] Therefore, there is great interest to develop new methods for degrading picloram in water, in cases where the photodegradation process is not a viable option.

In this sense, a detailed study of the reactivity exhibited by picloram at the molecular level may become fundamental to understand its degradation mechanism. Only few theoretical studies have analyzed the electronic properties of picloram. However, such studies were focusing to relate the molecular structure of picloram with its antibody and auxinic activities.[28,29] To the best of our knowledge, picloram reactivity, at the molecular level, has not been analyzed yet. Therefore, in this work we have analyzed the molecular reactivity of picloram through global and local reactivity descriptors derived from the Density Functional Theory (DFT).[30] We consider that this kind of study will contribute to get a better understanding of the chemical behavior in aqueous media of this herbicide.

Theory

Within the framework of the Density Functional Theory, it is possible to define universal concepts of molecular structure stability and reactivity through global and local reactivity parameters. Note that even when these reactivity parameters were derived from DFT, they may be employed to analyze the reactivity at other levels of theory.[30-32] These global reactivity parameters are the electronic chemical potential (μ), the electronegativity (χ) and hardness (η) which may be defined as:[30-32]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(r)} = -\frac{1}{2}\left(I - A\right) \tag{1}$$

$$\chi = -\mu \tag{2}$$

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{\nu(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} = \left(I - A\right) \tag{3}$$

In these equations E, N, and $\nu(r)$ are the energy, number of electrons and the external potential of the system, respectively while I is the vertical ionization energy and A stands for the vertical electron affinity. The energy value of the vertical electronic affinity is calculated as $A = E(N) - E(N+1)$ where $E(N)$ and $E(N+1)$ are the total ground-state energies in the neutral *N* and singly charged (N+1) configurations while the vertical ionization energy can be evaluated through $I = E(N-1) - E(N)$. The chemical potential measures the escaping tendency of an electron and it is minus the Mulliken electronegativity of molecules,[33] while η is related to the molecular polarizability.[34,35] Additional to μ, χ and η, the global electrophilicity index ω was defined by Parr and it can be calculated using μ and η:[36]

$$\omega = \frac{\mu^2}{2\eta} \tag{4}$$

According to this definition ω measures the susceptibility of chemical species to accept electrons. Thus, low values of ω suggest a good nucleophile while higher values indicate the presence of good electrophiles.[36]

Additional to the global reactivity parameters, it is possible to

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define local reactivity parameters which can be used to analyze the reactivity on different sites within a molecule. In this sense, the Hard and Soft Acids and Base principle (HSAB) has been useful to predict the reactivity of chemical systems.[30,37-42] Thus, from HSAB principle in combination with the Density Functional Theory, it has been possible to identify many useful and important reactivity concepts such as the Fukui Function ($f(\vec{r})$).[30] The Fukui function is defined as:[30]

$$f(\bar{r})=\left(\frac{\partial\rho(\bar{r})}{\partial N}\right)_{v(r)}=\left(\frac{\partial\mu(\bar{r})}{\partial v(r)}\right) \qquad (5)$$

where $\rho(\bar{r})$ is the electronic density. This function allows identifying the preferred regions where a chemical species will alter its electronic density when the number of electrons is modified. Thus, this function indicate the susceptibility of the electronic density to be deformed at a given position upon accepting or donating electrons.[30,39,40] Also, it is important to highlight that sites in chemical species with the largest values of $f(\bar{r})$ are those with higher reactivity.[43,44] The corresponding condensed or atomic Fukui functions (FF) on the *j*th atom site can be evaluated through the following equations:[30]

$$f_j^- = q_j(N) - q_j(N-1), \qquad (6)$$

$$f_j^+ = q_j(N+1) - q_j(N), \qquad (7)$$

$$f_j^0 = \frac{1}{2} q_j[(N+1) - q_j(N-1)] \qquad (8)$$

for electrophilic $f_j^-(r)$, nucleophilic $f_j^+(r)$ or free radical $f_j^0(r)$ attacks, on the reference molecule, respectively. In these equations, q_j is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the j_{th} atomic site in the neutral (N), anionic (N + 1) or cationic (N – 1) chemical species.

METHODOLOGY

The optimal conformations of picloram were subjected to full geometry optimization in the gas phase employing the hybrid functional B3LYP[45-47] and the basis set 6-311++G(2d,2p).[48,49] The optimized molecules in the gas phase were further reoptimized at the B3LYP/6-311++G(2d,2p) level employing the PCM solvation model.[50,51] The vibrational frequencies were computed to make sure that the stationary points were minima in the potential energy surface. Finally, the optimized B3LYP/6-311++G(2d,2p) geometries were reoptimized employing the second order Moller Plesset theory (MP2)[52] with the basis set 6-311++G(2d,2p) in the aqueous phase. The final atomic charges for picloram species have been obtained in the framework of MP2 theory, in all the calculations of these atomic charges, the option DENSITY=MP2 was used. All the calculations here reported were performed with the package Gaussian 09[53] and visualized with the GaussView V. 2.08[54] and Gabedit[55] packages.

RESULTS AND DISCUSSION

It has been reported that in aqueous solution, picloram may exist as unionized acid or neutral (Figure 1a), deprotonated or anionic (Figure 1b), cationic (Figure 1c) and dipolar (Figure 1d) forms.[56] At 4.2 < pH < 4.8 the anionic form is predominant while the dipolar and cationic forms are in major proportion at 0.2 < pH < 2.8, while at other pH values the neutral form is predominant.[56]

The structures depicted in Figure 1, were optimized at the B3LYP/6-311++G (2d,2p) level in the gas phase. In order to analyze the effect of solvation on the electronic properties of picloram forms, the optimized structures in the gas phase were used as starting point to reoptimize them at the B3LYP/6-311++G(2d,2p) level without any symmetry constraints and employing the PCM solvation model. The calculated solvation energies were 8.2, 19.7, 48.4 and 59.9 kcal mol^{-1} for neutral, dipolar, cationic and anionic species, respectively. Last values suggest that the anionic and cationic species require bigger solvation energy to be stabilized in solution, in comparison to neutral and dipolar forms of picloram. A frequency analysis was carried out to verify that the optimized geometries are minimums, in all cases the frequency values were positive. A summary of the main bands for each picloram form is depicted in Figures 2 and 3. The IRs for neutral and cationic forms of picloram are reported in Figure 2. Note the presence of two main bands at 3380 and 3480 cm^{-1} approximately which correspond to N-H-stretching vibrations. Adjacent to these bands are the peaks centered around 3700 cm^{-1} related to OH stretching vibrations. The carbonyl stretching frequency was observed at 1760 cm^{-1}. For anionic and dipolar forms, see Figure 3, N-H-stretching vibrations were observed in the range 3600-3700 cm^{-1} while the carbonyl stretching vibration was detected in the zone 1600-1680 cm^{-1} respectively. The typical C=C pyridine ring vibrations were observed in the range 1300-1550 cm^{-1}. It is important

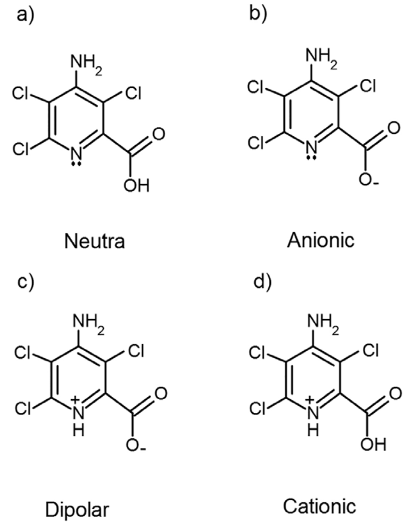

Figure 1. *Picloram species in solution a) Neutra, b) Anionic, c) Cationic and d) Dipolar [5]*

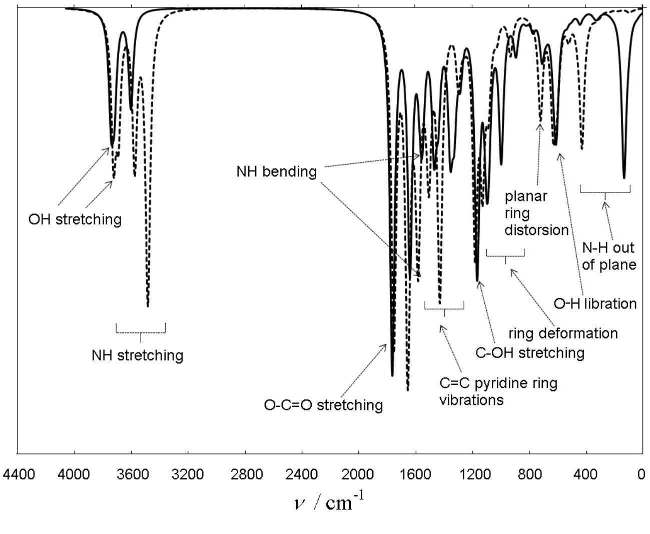

Figure 2. *Theoretical IR spectra of neutra (solid line) and cationic (broken line) forms of picloram in aqueous phase obtained at the B3LYP/6--311++G(2d,2p) level*

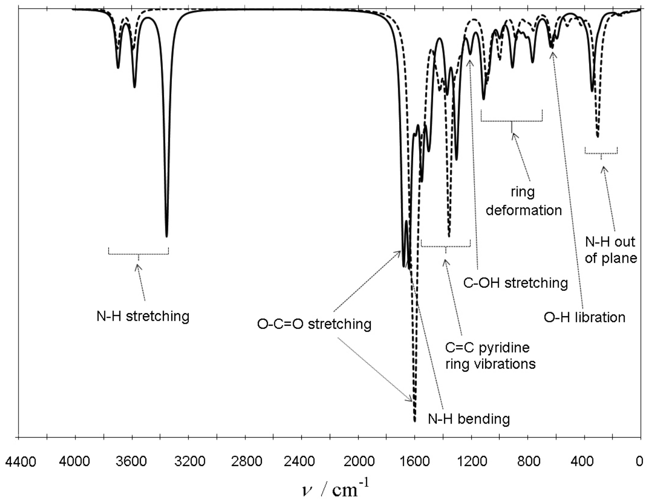

Figure 3. Theoretical IR spectra of dipolar (solid line) and anionic (broken line) forms of picloram in aqueous phase obtained at the B3LYP/6-311++G(2d,2p) level

to mention that these frecuency values are in agreement with those reported in the literature.[57]

The structures optimized at the B3LYP/6-311++G(2d,2p) level were further reoptimized at the MP2/6-311++G(2d,2p) level in the aqueous phase, see Figure 4. MP2 calculations were carried out in order to improve the evaluation of the energy correlation calculated at the B3LYP/6-311++G(2d,2p) level. The bond distances and angles obtained at the MP2 level were very similar to those obtained at the DFT level. The solvation energies for neutral, dipolar, cationic and anionic species evaluated at the MP2 level were 7.7, 17.6, 47.9, 60.8 kcal mol^{-1} respectively. Note that, in comparison with the MP2 results, the values of the solvation energy are overestimated by B3LYP. Moreover, the accepted value of the solvation energy for picloram in its neutral form is 7.5 ± 0.2 kcal mol^{-1}.[56] Last value compare favorably with the obtained at the MP2 level. This result suggests that MP2 calculations are more reliable than B3LYP calculations to evaluate the molecular properties of picloram.

Global reactivity descriptors

Global Reactivity descriptors were evaluated at the levels of theory B3LYP/6-311++G(2d,2p) and MP2/6-311++G(2d,2p). The values of μ, η, ω were calculated employing the equations 1, 3 and 4 respectively (Table 1). At the MP2 level, the hardness values are following the order cationic > neutra > dipolar > anionic. Last result suggests that the the cationic form is the most stable specie. The electrophilicity follows the tendency anionic > dipolar > neutra > cationic. Note that, the anionic form of picloram exhibits a major nucleophilic behavior than the other picloram forms. Also, it is clear that the values of the global reactivity parameters depend on the level of theory used. Thus, it is possible to conclude that the evaluation of the energy correlation through MP2 calculations should increase the accuracy on the global reactivity parameters calculated for picloram species.

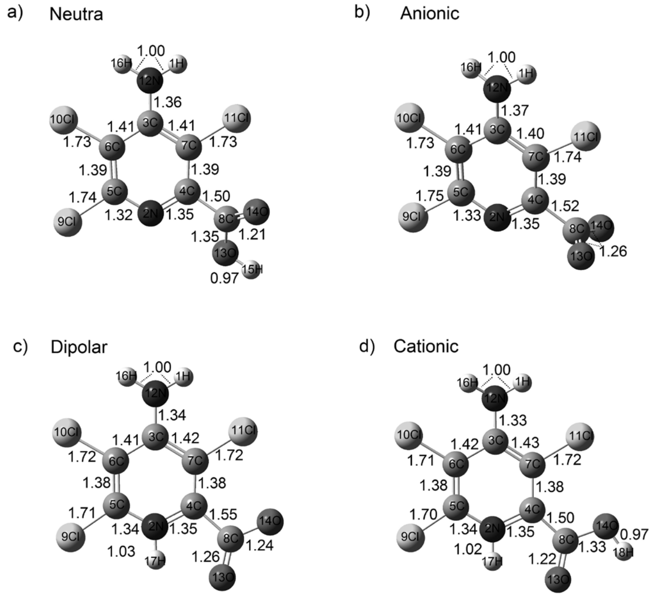

Figure 4. Picloram species in solution a) Neutra (Dihedral Angle 2N-4C-8C-13O=38.14°), b) Anionic (Dihedral Angle 2N-4C-8C-13O=-89.75°), c) Cationic (Dihedral Angle 2N-4C-8C-13O=0°) and d) Dipolar (Dihedral Angle 2N-4C-8C-13O=0°). All structures were optimized at MP2/6-311++G(2d,2p) level of theory. Bond distances (Å) are labeled in each Figure. The dipole electric moments for neutral, anionic, cationic and dipolar forms evaluated at the MP2 level were 4.78, 11.95, 4.15 and 15.27 Debyes respectively

Local reactivity descriptors

In order to determine the pin point distribution of the active sites of the picloram species; we employed the equations 6, 7 and 8 to calculate the Fukui function values. It is important to highlight that the values of FF are dependent on the scheme of charges used. In this sense, atomic charges derived from the electrostatic potential have found good acceptation to calculate the condensed Fukui function and a good agreement with the experimental results has been obtained.[58] We report the values of the Fukui function obtained for picloram in its neutral form (Table 2). These values were evaluated through the atomic charges derived from electrostatic potential (MEP) which were calculated at two levels of theory B3LYP/6-311++G(2d,2p) and MP2/6-311++G(2d,2p). We carried out these calculations in order to compare the results provided by the B3LYP hybrid functional with those given by more sophisticated level of calculations as MP2 theory. The same procedure was done to evaluate the values of the FF for anionic (Table 3), cationic (Table 4) and dipolar (Table 5) species.

For neutral form (Table 2), observe that at the DFT level the most susceptible site to an electrophilic attack is located on 12N. In the case of a nucleophilic attack, the most reactive site is on 4C. For a free radical attack the most reactive site is on 12N. At the

Table 1. Global reactivity descriptors for picloram at the B3LYP/6-311++G(2d,2p) and MP2/6-311++G(2d,2p) levels of theory

	B3LYP/6-311++G(2d,2p)					MP2/6-311++G(2d,2p)				
	I / eV	A / eV	η / eV	μ / eV	ω / eV	I / eV	A / eV	η / eV	μ / eV	ω / eV
Neutra	-6.92	2.37	9.29	2.28	0.28	-8.59	1.75	10.34	3.42	0.56
Anionic	-6.35	1.09	7.44	2.63	0.46	-8.26	0.33	8.58	3.96	0.92
Dipolar	-7.26	2.49	9.75	2.38	0.29	-8.81	1.37	10.18	3.72	0.68
Cationic	-7.72	3.43	11.15	2.14	0.21	-9.22	3.02	12.24	3.10	0.39

Table 2. Values of the condensed Fukui function for neutral picloram form computed from MEP charges according to the equations (6)-(8)

Atom	B3LYP/6-311++G(2d,2p)			MP2/6-311++G(2d,2p)		
	f^-	f^+	f^0	f^-	f^+	f^0
1H	-0.011	0.012	0.001	0.003	0.009	0.006
2N	0.149	0.066	0.107	0.147	***0.300***	0.223
3C	-0.015	0.083	0.034	0.048	-0.104	-0.028
4C	0.084	***0.151***	0.118	0.068	-0.173	-0.052
5C	-0.020	0.014	-0.003	-0.034	-0.079	-0.057
6C	0.051	0.013	0.032	0.042	0.232	0.137
7C	0.032	-0.017	0.007	0.007	0.294	0.151
8C	-0.076	0.050	-0.013	-0.040	0.003	-0.018
9Cl	0.080	0.085	0.082	0.110	0.042	0.076
10Cl	0.131	0.124	0.127	0.127	0.182	0.155
11Cl	0.148	0.122	0.135	0.131	0.130	0.131
12N	***0.374***	0.042	***0.208***	***0.317***	0.004	***0.161***
13O	0.013	0.078	0.045	0.018	0.038	0.028
14O	0.048	0.141	0.094	0.033	0.090	0.062
15H	0.024	0.027	0.026	0.021	0.025	0.023
16H	-0.012	0.008	-0.002	0.001	0.006	0.004

Table 3. Values of the condensed Fukui function for anionic picloram form computed from MEP charges according to the equations (6)-(8)

Atom	B3LYP/6-311++G(2d,2p)			MP2/6-311++G(2d,2p)		
	f^-	f^+	f^0	f^-	f^+	f^0
1H	0.011	0.002	0.007	0.005	-0.011	-0.003
2N	0.056	***0.181***	0.118	0.169	0.125	0.147
3C	-0.006	0.040	0.017	0.077	0.004	0.041
4C	0.091	0.116	0.104	0.057	-0.091	-0.017
5C	-0.005	-0.010	-0.008	-0.034	-0.023	-0.028
6C	0.059	0.047	0.053	0.037	0.184	0.111
7C	0.029	0.059	0.044	0.003	***0.267***	0.135
8C	-0.210	-0.149	-0.179	-0.088	-0.064	-0.076
9Cl	0.090	0.094	0.092	0.116	0.191	0.154
10Cl	0.098	0.138	0.118	0.121	0.021	0.071
11Cl	0.109	0.090	0.100	0.123	0.187	0.155
12N	0.028	0.157	0.092	***0.268***	0.164	***0.216***
13O	***0.324***	0.118	***0.221***	0.070	0.015	0.042
14O	0.322	0.115	0.219	0.070	0.011	0.041
16H	0.005	0.001	0.003	0.006	0.020	0.013

Table 4. Values of the condensed Fukui function for cationic picloram form computed from MEP charges according to the equations (6)-(8)

Atom	B3LYP/6-311++G(2d,2p)			MP2/6-311++G(2d,2p)		
	f^-	f^+	f^0	f^-	f^+	f^0
1H	0.016	0.022	0.019	0.029	0.024	0.027
2N	0.162	-0.013	0.074	0.000	-0.035	-0.017
3C	0.003	0.126	0.064	0.110	0.100	0.105
4C	0.052	***0.221***	0.136	0.115	***0.230***	0.172
5C	-0.033	0.067	0.017	0.060	0.093	0.076
6C	0.092	-0.043	0.024	0.024	0.000	0.012
7C	0.027	-0.039	-0.006	-0.052	-0.056	-0.054
8C	-0.055	0.050	-0.002	-0.027	0.033	0.003
9Cl	0.091	0.074	0.083	0.116	0.061	0.089
10Cl	0.173	0.103	0.138	0.149	0.095	0.122
11Cl	0.133	0.117	0.125	0.134	0.085	0.109
12N	***0.254***	0.059	***0.157***	***0.253***	0.105	***0.179***
13O	0.052	0.135	0.093	0.016	0.137	0.076
14O	0.014	0.045	0.029	0.018	0.050	0.034
16H	0.014	0.019	0.017	0.028	0.014	0.021
17H	-0.012	0.026	0.007	0.008	0.041	0.025
18H	0.018	0.031	0.025	0.018	0.024	0.021

Table 5. Values of the condensed Fukui function for dipolar picloram form computed from MEP charges according to the equations (6)-(8)

Atom	B3LYP/6-311++G(2d,2p)			MP2/6-311++G(2d,2p)		
	f^-	f^+	f^0	f^-	f^+	f^0
1H	0.047	0.026	0.037	0.031	0.025	0.028
2N	0.077	0.044	0.061	0.060	0.037	0.048
3C	0.068	0.134	0.101	0.101	0.034	0.068
4C	-0.056	***0.227***	0.085	0.111	***0.194***	0.153
5C	-0.017	0.074	0.029	0.017	0.097	0.057
6C	-0.005	-0.044	-0.025	0.004	0.064	0.034
7C	0.001	-0.048	-0.024	-0.019	0.052	0.017
8C	-0.115	-0.039	-0.077	-0.074	-0.066	-0.070
9Cl	0.045	0.096	0.071	0.110	0.078	0.094
10Cl	0.041	0.098	0.070	0.129	0.075	0.102
11Cl	0.096	0.085	0.090	0.128	0.061	0.095
12N	-0.046	0.118	0.036	***0.257***	0.145	***0.201***
13O	0.291	0.098	0.194	0.071	0.081	0.076
14O	***0.568***	0.101	***0.334***	0.060	0.091	0.075
16H	0.019	0.019	0.019	0.028	0.018	0.023
17H	-0.014	0.012	-0.001	-0.017	0.014	-0.001

MP2/6-311++G(2d,2p) level, the reactivity order is 12N, 2N and 2N for electrophilic, nucleophilic and free radical attacks, respectively. Thus, according to the MP2 level the more reactive sites are located on the nitrogen atoms.

For the anionic specie (Table 3), at the DFT level the most susceptible sites to electrophilic, nucleophilic and free radical attacks are 13O, 2N and 13O, respectively. At the MP2 level the more reactives sites are 12N, 7C and 12N for electrophilic, nucleophilic and free radical attacks. In the case of the cationic form (Table 4), the more susceptible sites to electrophilic, nucleophilic and free radical attacks are 12N, 4C and 12N, in that order. This result is coincident in both DFT and MP2 levels of theory. Finally, for the dipolar specie at the DFT level the most susceptible site to electrophilic attacks is located on 14O, (see Table 5). In the case of nucleophilic attacks, the most reactive site is on 4C. For free radical attacks the most reactive site is on 14O. The calculations at the MP2 level predict that the most electrophilic site is located on 12N. In the case of nucleophilic attacks the most reactive site is on 4C and a free radical attacks are more probable on 12N.

Note that in most of the cases B3LYP was unable to predict the results obtained at the MP2 level. According to the results obtained at the MP2 level the more reactive sites for electrophilic and free radical attacks are on the nitrogen in the pyridine ring. The more reactive sites for nucleophilic attacks are located on 2N, 7C, 4C and 4C for Neutral, Anionic, Cationic and Dipolar forms respectively. These results suggest that a change in the pH solution modifies the nucleophilic behavior of picloram while its electrophilic and free radical behavior remains unaltered. Thus, electrophiles and free radicals will react on the pyridin nitrogen at different pH values. Nucleophilic attacks on the anionic form will cause dechlorination on 7C. On the other hand, nucleophilic attacks on cationic and dipolar forms would cause decarboxylation. These results are in agreement with the possible pathways reported for picloram degradation which are decarboxylation or amino displacement,[59,60] and dechlorination process.[59,61]

CONCLUSIONS

At the MP2 level the more reactives sites for electrophilic and free radical attacks are on the pyridine nitrogen atom. Nucleophilic attacks on anionic picloram will cause a dechlorination while a decarboxylation is expected on the cationic and dipolar forms. The B3LYP functional can predict adequately the geometries of picloram forms. However, this functional fails to evaluate satisfactorily the electronic energies for picloram species causing an incorrect evaluation of the global and local reactivity parameters. Thus, MP2 calculations are necessary to evaluate the picloram reactivity.

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