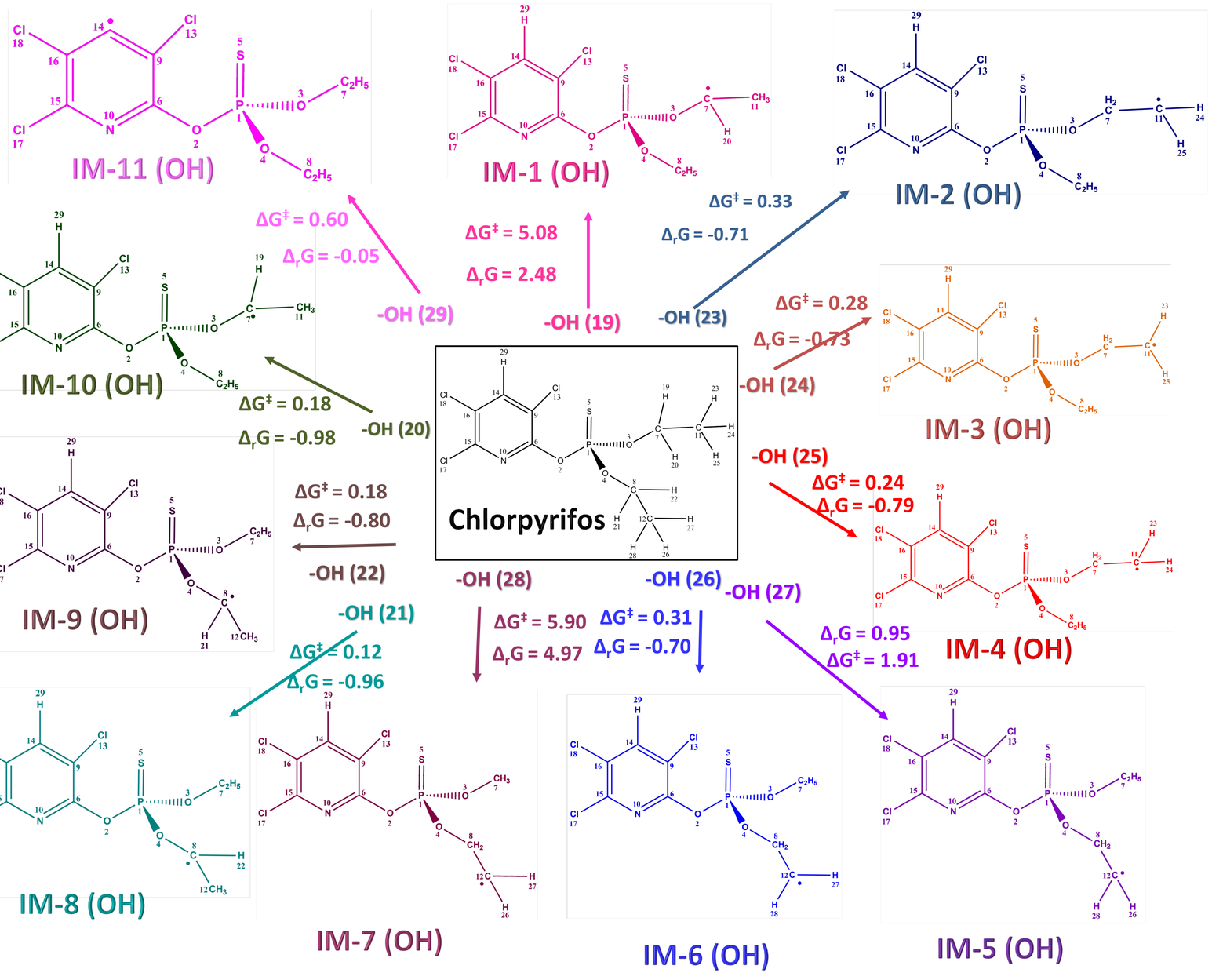
Theoretical Investigation of Plasma Induced Degradation of Chlorpyrifos

Introduction

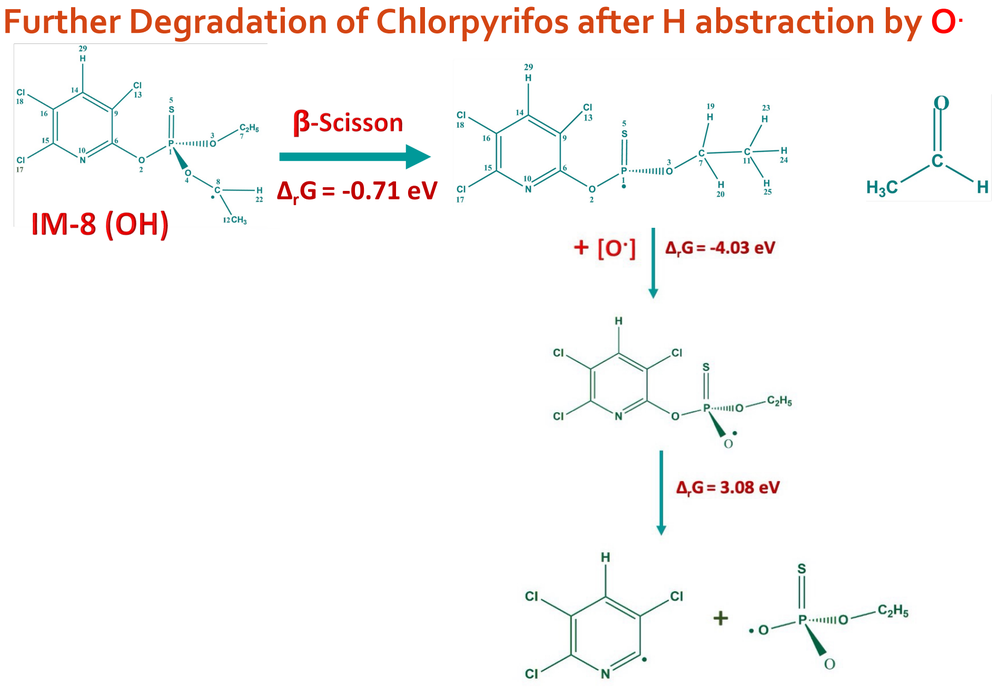
- Chlorpyrifos, a commonly used pesticide, poses serious health risks to humans, animals and the environment.
- To reduce the toxic impact of chlorpyrifos, its degradation into less harmful substances is of high importance.
- Plasma assisted degradation is a promising, eco-friendly method that effectively breaks down chlorpyrifos using reactive species ($O^{\cdot}$,$N^{\cdot}$,$OH^{\cdot}$,$H^{+}(H_2O)_{n=3,4}$,...).
- Quantum chemical calculations of all the reactions involved in this work were performed using Density Functional Theory (DFT) with Gaussian 16 software package.

Degradation of Chlorpyrifos by $O^{\cdot}$



Gibb's free energy of activation ($\Delta G^{‡}$) and Gibb's free energy change of a reaction ($\Delta_r G$) in eV at 298K for the H abstraction pathways of chlorpyrifos with $O^{\cdot}$ calculated at M062X/6-311++G(d,p) level of theory.

Further Degradation of Chlorpyrifos after H abstraction by $O^{\cdot}$



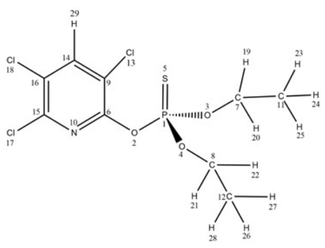
Degradation of Chlorpyrifos by $H^{+}(H_2O)_{n=3,4}$ & $NH_4^{+}(H_2O)_{n=3,4}$

$$\text{Chlorpyrifos} + \underset{(Y= H,\ NH_4)}{Y^{+}(H_2O)_{n=3,4}} \longrightarrow \text{Chlorpyrifos}\ (H^{+}) + Y(H_2O)_{n=3,4}$$

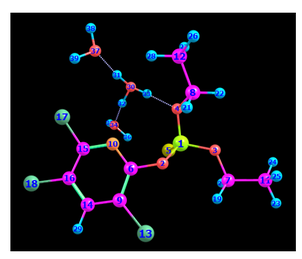
Reactant Ion	PBE (eV)
$H^{+}(H_2O)_3$	8.79
$H^{+}(H_2O)_4$	9.07
$NH_4^{+}(H_2O)_3$	9.83
$NH_4^{+}(H_2O)_4$	10.5

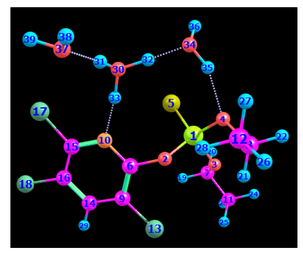
PBE – Proton Binding Energy

Protonation Site	Proton Affinity (eV)
N	8.97
C-6 (C6→N)	8.97
C-9	9.54
C-14	6.70
C-15	6.83
C-16	7.50
O-2 (O2→N)	8.97
O-3	8.03
O-4 (O4→N)	9.05
P (P →N)	9.05
S	8.82



Attachment Site	Attachment of $H^{+}(H_2O)$ to Chlorpyrifos (Cp) {Cp + $H^{+}(H_2O)_3$ -> Cp $H^{+}(H_2O)_3$}	
C-14 (c-14 -> O_4)	$\Delta_r G$ = -0.04 ev	$\Delta_r H$ = -1.20
C-15 (c-15 -> N)	$\Delta_r G$ = -0.26 ev	$\Delta_r H$ = -1.25
C-16 (c-16 -> N)	$\Delta_r G$ = -0.21 ev	$\Delta_r H$ = -1.23
C-6	$\Delta_r G$ = 0.21 ev	$\Delta_r H$ = -0.98
C-9 (c-9 -> O_4)	$\Delta_r G$ = -7.14 ev	$\Delta_r H$ = -8.56
N (Bridge between N & O_4)	$\Delta_r G$ = -0.19 ev	$\Delta_r H$ = -1.22
O-2 (Bridge between N & O_2)	$\Delta_r G$ = 0.48 ev	$\Delta_r H$ = -0.84
O-3 Bridge between N & O_3)	$\Delta_r G$ = 0.28 ev	$\Delta_r H$ = -0.99
O-4	$\Delta_r G$ = 1.26 ev	$\Delta_r H$ = -0.07
P	$\Delta_r G$ = -2.58 ev	$\Delta_r H$ = -3.88
S	$\Delta_r G$ = -2.58 ev	$\Delta_r H$ = -3.78





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2. John, E. M., & Shaike, J. M. (2015). Chlorpyrifos: pollution and remediation. In *Environmental Chemistry Letters* (Vol. 13, Issue 3, pp. 269–291).

Acknowledgement

- This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-22-0522 and the Slovak Grant Agency for Science (contract no. VEGA 1/0553/22).
- Funded by the EU Next Generation EU through the Recovery and Resilience Plan for Slovakia under the project No. 09l01-03-V04-00047.
- This work was supported in part through the Comenius University in Bratislava CLARA@UNIBA.SK high-performance computing facilities, services and staff expertise of Centre for Information Technology (https://uniba.sk/en/HPC-Clara).

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