

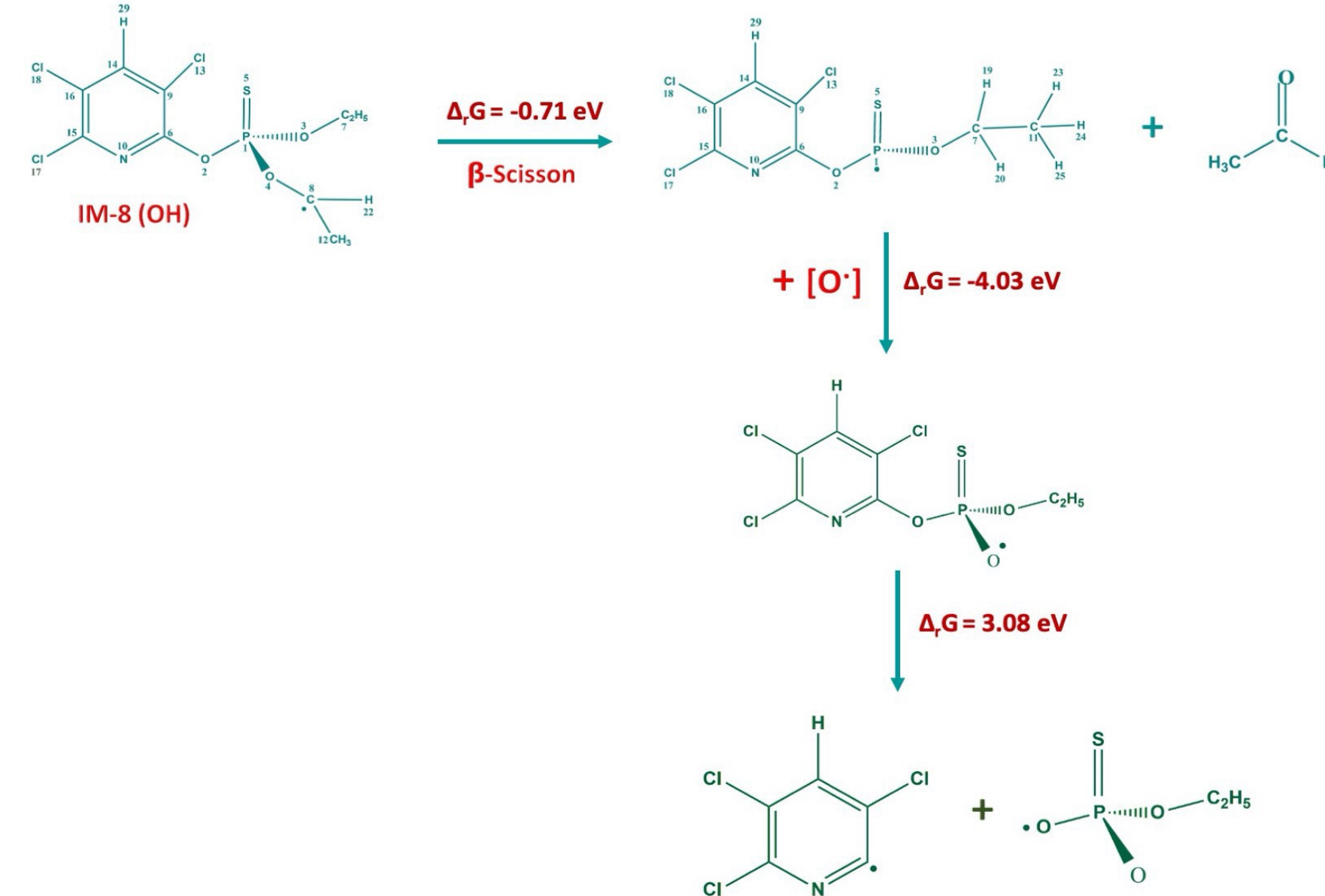
Theoretical Investigation of Plasma Induced Degradation of Chlorpyrifos



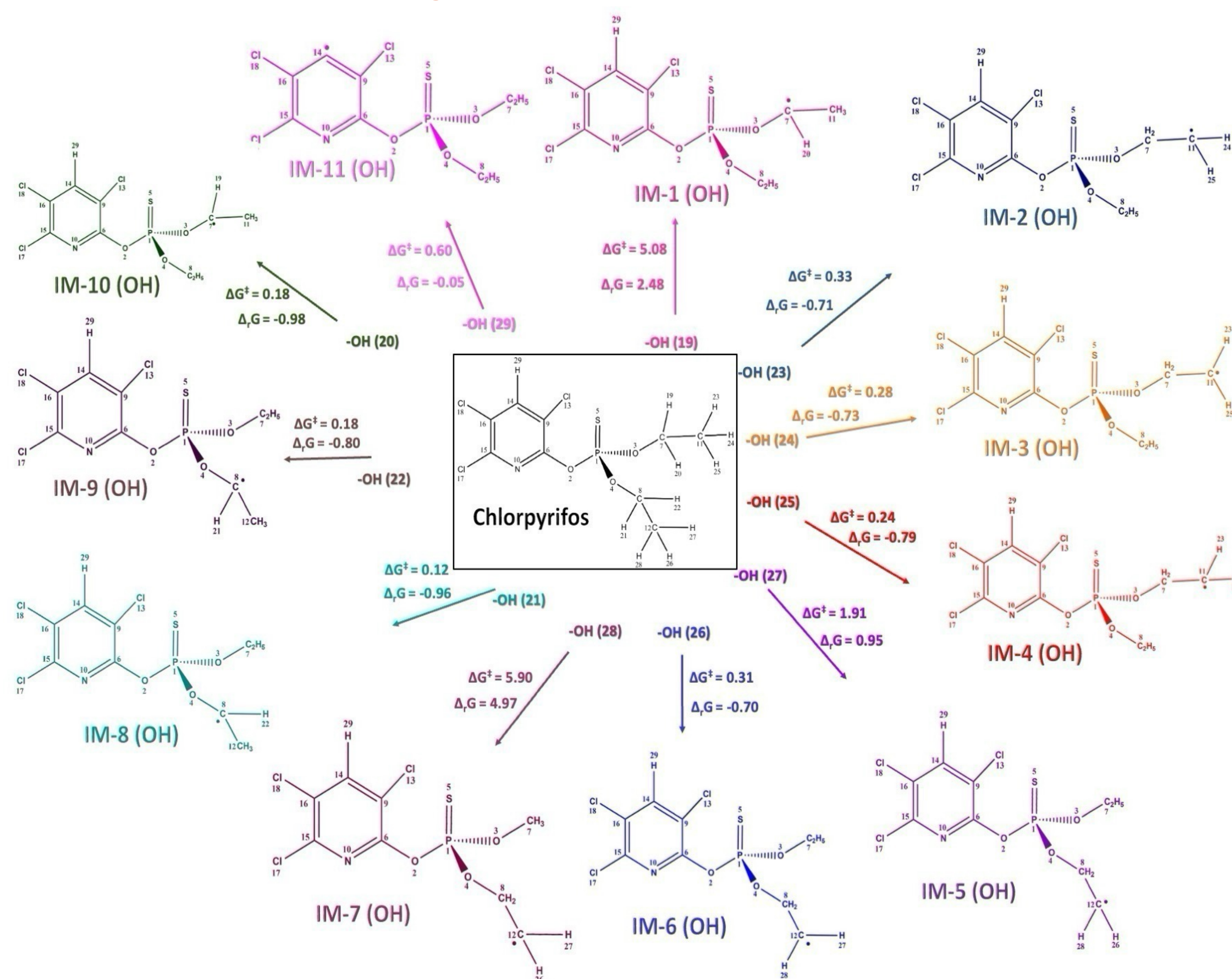
Introduction

- 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 ($O^{\cdot-}$, $N^{\cdot-}$, $OH^{\cdot}$, $H^+(H_2O)_{n=3,4}, \dots$).
- Quantum chemical calculations of all the reactions involved in this work were performed using Density Functional Theory (DFT) with Gaussian 16 software package.

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

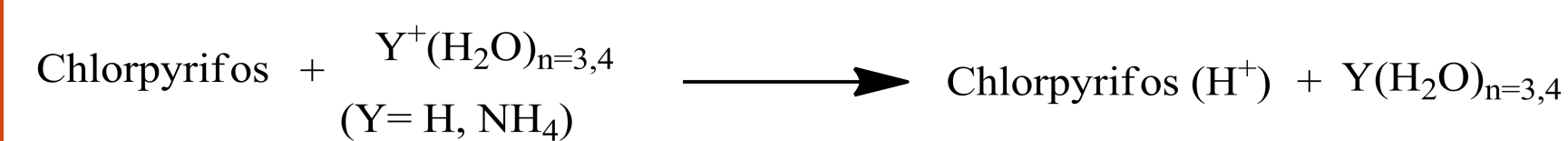


Degradation of Chlorpyrifos by $O^{\cdot-}$



Gibb's free energy of activation ($\Delta G^{\ddagger}$) 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.

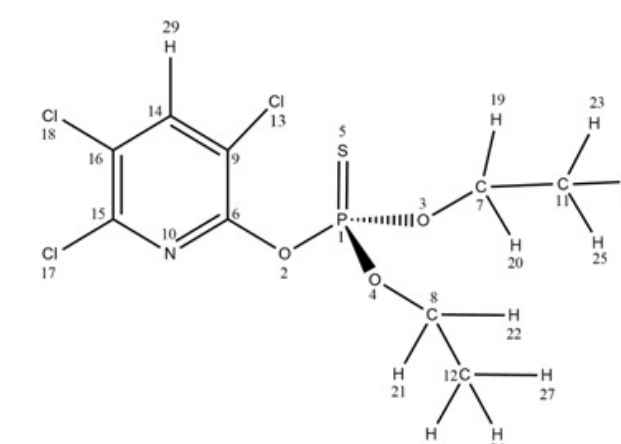
Degradation of Chlorpyrifos by $H^+(H_2O)_{n=3,4}$ & $NH_4^+(H_2O)_{n=3,4}$



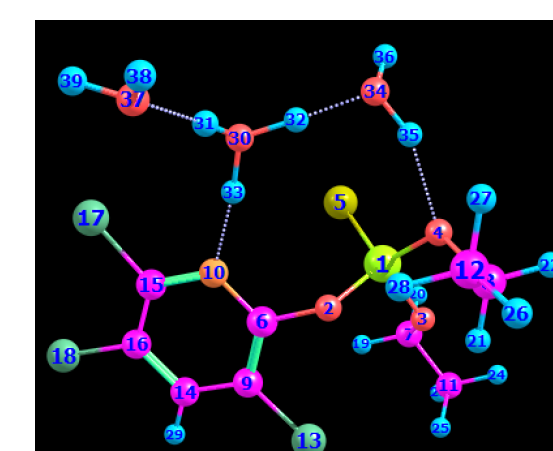
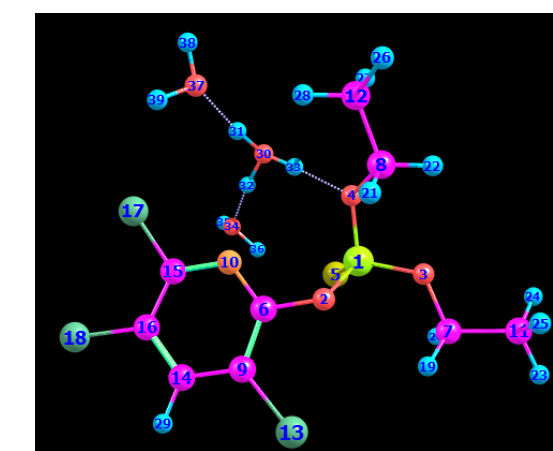
Reactant Ion	PBE (eV)
$H^+(H_2O)_3$	8.79
$H^+(H_2O)_4$	9.07
$NH_4^+(H_2O)_3$	9.83
$NH_4^+(H_2O)_4$	10.5

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 $H^+(H_2O)_n$ to Chlorpyrifos (Cp) [$Cp + H^+(H_2O)_n \rightarrow Cp H^+(H_2O)_n$]	
C-14 (c-14 → O4)	$\Delta_r G = -0.04 \text{ eV}$	$\Delta_r H = -1.20$
C-15 (c-15 → N)	$\Delta_r G = -0.26 \text{ eV}$	$\Delta_r H = -1.25$
C-16 (c-16 → N)	$\Delta_r G = -0.21 \text{ eV}$	$\Delta_r H = -1.23$
C-6	$\Delta_r G = 0.21 \text{ eV}$	$\Delta_r H = -0.98$
C-9 (c-9 → O4)	$\Delta_r G = -7.14 \text{ eV}$	$\Delta_r H = -8.56$
N (Bridge between N & O4)	$\Delta_r G = -0.19 \text{ eV}$	$\Delta_r H = -1.22$
O-2 (Bridge between N & O2)	$\Delta_r G = 0.48 \text{ eV}$	$\Delta_r H = -0.84$
O-3 (Bridge between N & O3)	$\Delta_r G = 0.28 \text{ eV}$	$\Delta_r H = -0.99$
O-4	$\Delta_r G = 1.26 \text{ eV}$	$\Delta_r H = -0.07$
P	$\Delta_r G = -2.58 \text{ eV}$	$\Delta_r H = -3.88$
S	$\Delta_r G = -2.58 \text{ eV}$	$\Delta_r H = -3.78$



References

- Bose, S.; Kumar, P.S.; Dai-Viet, N.V. A review on the microbial degradation of chlorpyrifos and its metabolite TCP. *Chemosphere* 2021, 283, 131447.
- John, E. M., & Shaik, 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>).



FAKULTA MATEMATIKY,
FYZIKY A INFORMATIKY
Univerzita Komenského
v Bratislave

MATFYZ
CONNECTIONS

Navya Arepalli, Alexandra Jančíšínová,
Štefan Matejčík, Peter Papp

Department of Experimental Physics, Comenius University in
Bratislava, Mlynská dolina F2, 842 48 Bratislava, Slovakia.