

Computational Modeling of 2-Monochlorophenol and 2-Monochlorothiophenol

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Abstract

Substituted phenolic compounds are well established organic contaminants in the atmosphere and natural ecosystems. They are implicated in a variety of health problems such as oxidative stress, cancer and respiratory diseases. Although the chemistry of 2-monochlorophenol is extensively studied experimentally, theoretical studies on this molecule especially on its thermal degradation is scarce in literature. The goal of this investigation is to investigate not only the thermal properties of 2-monochlorophenol and 2-monochlorothiophenol but also their electronic properties from a theoretical stand point. To simulate the thermolysis of these pollutants under conditions representative of municipal waste incineration, a temperature range of 300-1000°C at typical increments of 100 °C at 1 atmosphere was used. Gaussian 03 computational suite of programs was employed in this study. The density functional theory (DFT) in conjunction with B3LYP correlation function and a variety of basis sets were employed in this investigation. Two basis sets normally selected for molecular modeling of polar organic molecules; 6-31+G and 6-31G+(d,p) have been given priority in this work. Thermochemical results show that 2-mochlorothiophenol easily dissociates to 2-monochlorothiophenoxy radical in comparison to the dissociation of 2-monochlorophenol to 2-monochlorophenoxy radical in the whole range of pyrolysis temperature. At 298 K at 1 atmosphere, the change in enthalpy for the formation of 2-monochlorothiophenoxy and 2-monochlorophenoxy radicals was respectively, 70.78 and 85.18 kcal mol⁻¹. The toxicities of these combustion by-products have also been reported in this study. It is evident that the substituent to the aromatic ring has a significant influence on the bond-dissociation energy. Molecular orbital profiles determined using Chemissian showed that 2-monochlorothiophenol is significantly nucleophilic whereas 2-monochlorophenol is electrophilic.

Key Words: free radicals, municipal waste incineration, thiophenol, toxicity

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Introduction

Chlorophenol compounds and their derivatives are ubiquitous pollutants in the environment. These compounds are introduced into the environment as a result of chemical and pharmaceutical industry activities (Igbinosa *et al.*, 2013). The widespread presence of chlorophenols in the ecosystem is also related with the production, use and degradation of numerous pesticides such as chlorinated cyclohexanes (Abhilash & Singh, 2008) and chlorobenzene (Balcke *et al.*, 2008). They accumulate in water, soil and air due to high stability, and impart an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes (Mahammad *et al.*, 2015). The two main processes that lead to phenol toxicity are unspecified toxicity related to hydrophobicity of the individual compound and the formation of free radicals (Michałowicz & Duda, 2007). The increase in hydrophobicity of chlorophenol is related to the increase in the number of chlorine atoms that enhances the toxicity of the individual compound (Boyd *et al.*, 2001). The compounds investigated in this study are presented in Fig. 1 (Modeled using HyperChem) (Leonid, 2012).

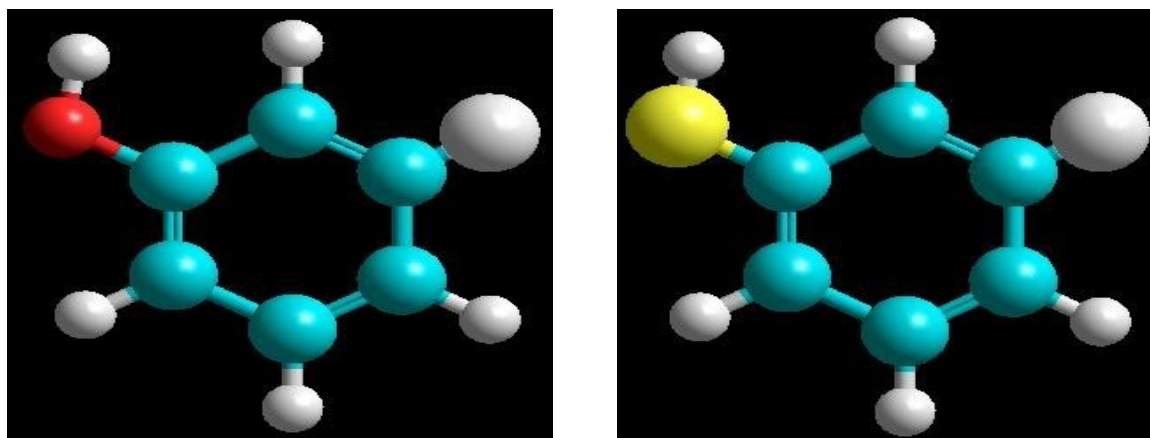


Fig.1: Molecular structures of 2-monochlorophenol (left) and 2-monochlorothiophenol (right)

The strength of the toxic influence of phenols results from the localization of the substituent. For example, a chlorine atom substituted in *ortho* position in phenol molecule decreases its toxicity and *meta* substitution increases the toxic action of the compound (Michałowicz & Duda, 2007). 2-monochlorophenol (2-MCP), a derivative of phenol is an organic compound which is used as a disinfectant agent, preservative and pesticide (Adane *et al.*, 2015; Shokufeh *et al.*, 2016). The sources of 2-monochlorophenol pollution are wastewaters from pesticide, solvent pharmaceuticals, paint and paper and pulp industries as well as water disinfecting processes (Joseph *et al.*, 2012; Muneer *et al.*, 2012). 2-MCP is toxic, poorly biodegradable and recalcitrant and has been classified as priority pollutant by United States protection agency (USEPA) (Ajeel *et al.*, 2015; Gonzalez *et al.*, 2015). It imposes hazardous health effects towards humans and animals (Darai & Kamali, 2014). This compound accumulates mostly in the kidney, liver, brain and muscles (Koumanova *et al.*, 2005). The signs and symptoms of 2-monochlorophenol toxicity include burning pain in mouth and throat, abdominal pain, vomiting and bloody diarrhea, headache, dizziness, weak irregular pulse, hypertension, possibly fleeting excitement and confusion followed unconsciousness and death resulting from respiratory, circulatory or cardiac failure (Cooper, 1996).

The toxic effects of 2-monochlorophenol include mutagenic and estrogenic effects (Jin *et al.*, 2016). Chlorothiophenols (CTPs) have widespread applications in manufacturing of dyes, pharmaceuticals, printing inks, insecticides, pesticides and polyvinylchloride (PVC) (Parette & Pearson, 2014). CTPs have been demonstrated to be the key intermediates or predominant precursors Polychlorinated thianthrene/dibenzothiophenes (PCTA/DTs) which are very toxic compounds (Fei *et al.*, 2015). CTPs are hazardous and toxic to human health and environment due to presence of chlorine and sulfur (Shi *et al.*, 2012). Studies indicate that the order of toxicity of CTPs increases with the degree of chlorination (Fei *et al.*, 2015; Ohashi *et al.*, 2005). Studies on the toxicological properties of 2-monochlorothiophenol is scarce in literature; however ingestion, inhalation and skin contact with this compound may cause severe injury or death. Contact with molten 2-monochlorothiophenol may cause severe burns to skin and eyes (Acros, 2015). 2-chlorothiophenol is a chlorinated thiophenol that is used in the manufacture of ink, dyes, pharmaceuticals and polymers such as PVC (Navarro *et al.*, 2008). 2-chlorothiophenol is also used in vulcanization process of rubber (Sullivan *et al.*, 2008). When these compounds and their corresponding free radicals are released into the environment, they have serious health environmental impacts.

Thermal degradation of 2-monochlorophenol and 2-chlorothiophenol yields a mixture of molecular compounds and their respective radicals; 2-monochlorophenoxy and 2-chlorothiophenoxy which are well-established environmental and human toxicants (Cheng *et al.*, 2012; Ohashi *et al.*, 2005). Toxicity to humans depends on dose exposure, duration, personal traits and habits (Ames *et al.*, 1987). Their toxicity is primarily due to hydrophobicity and tendency to form free organic radicals and reactive oxygen species. Most chlorophenols are carcinogenic and mutagenic (Dayan, 1993) and have been cited as the one of the root causes of increased mortality rate and chronic illnesses. They cause long term negative health effects and trigger diseases that are injurious to the human metabolic system.

This study investigates the thermochemistry and molecular models of 2-MCP and 2-MCTP from a theoretical perspective. The mechanistic degradation of these compounds to intermediate free radicals via various pathways has been presented in detail. Moreover, the molecular orbitals and electronic density maps have also been discussed in detail in relation to their toxicity. Experimental procedures used to probe electronic and thermal chemical properties such as bond angles and bond lengths of molecular structures are not elaborate enough and thus computational tools become indispensable.

Computational methodology

The thermochemical calculations and electronic properties of molecular compounds presented in this contribution were carried out using Gaussian 03 computational package (Frisch *et al.*, 2004; Ochterski, 2000). *Igor* software was used to interpret data graphically. The Density Functional Theory in conjunction with B3LYP/6-31+G theoretical level in addition to other basis sets (321G, 6-31G and 6-311G) (Becke, 1993; Lee *et al.*, 1988) was employed in this study. Furthermore, HyperChem software was used to obtain toxicity indices (Wójcik *et al.*, 2013). The change in enthalpy was determined using the conventional thermodynamic expression (equation 2) below.

$$\Delta_r H^0 = \sum \Delta_f H^0_{\text{products}} - \sum \Delta_f H^0_{\text{reactants}} \quad \text{Equation 1}$$

The change in Gibbs free energy at temperatures between 298 K and 1000 K for the two compounds was also calculated at 1 atmosphere.

Results and Discussion

To explore the effect of a given basis set on the internal energy of each species studied in this work. A graph of internal energy as a function of the basis set was generated (Fig. 2). It is evident that the larger basis set (6-311G) gave lower internal energies than all the other basis sets employed in this work. Although the internal energies of 2-monochlorophenol and 2-monochlorothiophenol were generally high, those of their respective radicals (2-monochlorophenoxy and 2-monochlorothiophenoxy radicals) were lower for all basis sets.

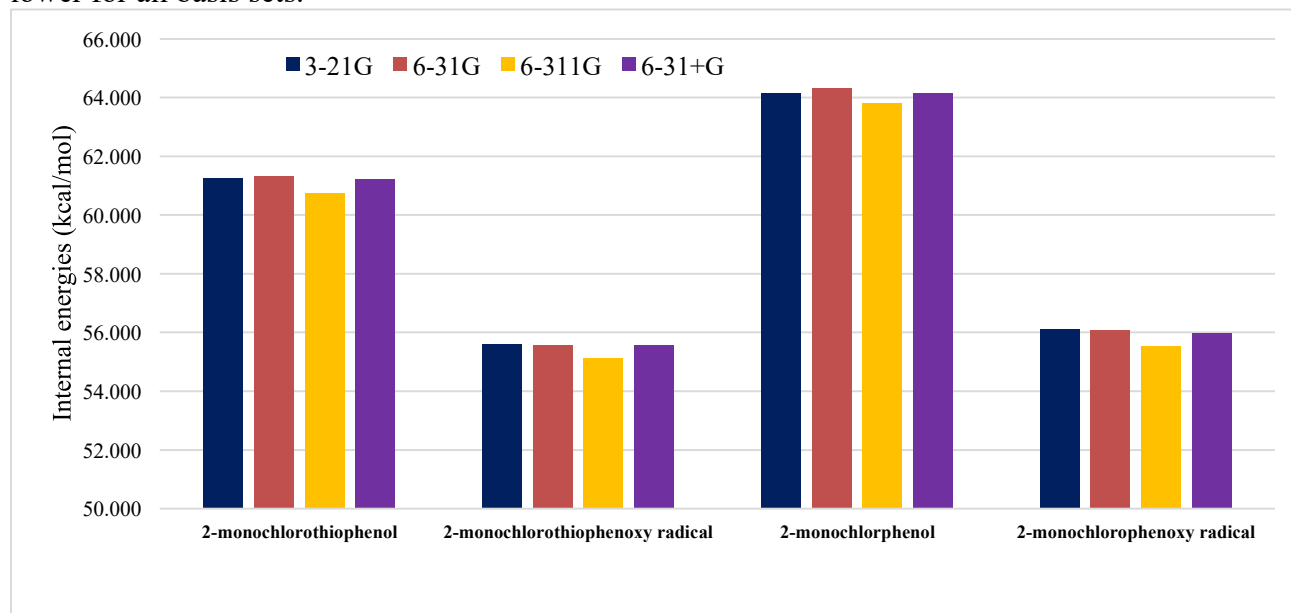


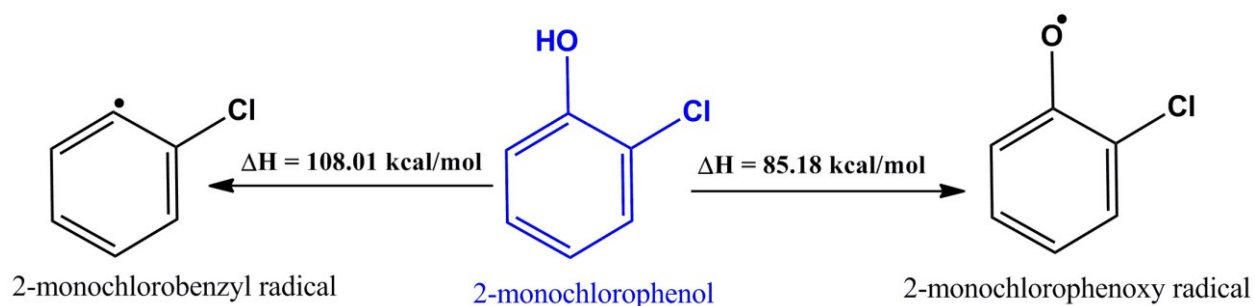
Fig 2: Variations in internal energies with different basis set

From a theoretical perspective, the 6-31+G basis is expected to give accurate results for most organic polar compounds because it takes into consideration the existence of hydrogen bonding. However, it is clear from the results presented in Fig. 1 that it deviates slightly from the results obtained when other basis sets (3-21G, 6-31G and 6-311G) are used. Remarkably therefore, the influence of basis set on internal energy of a species is not significant except when the basis set has a polarized character.

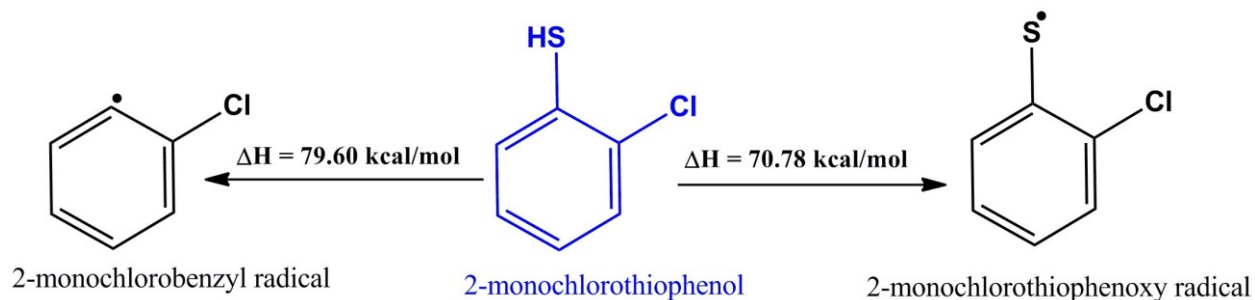
The proposed mechanistic pathways for 2-monochlorophenol and 2-monochlorothiophenol

Hydrogen abstraction is the most common event in the thermal degradation of environmental pollutants under conditions representative of municipal waste incineration. Scheme 1 gives the transformation of 2-monochlorophenol to 2-monochlorophenoxy radical while scheme 2 shows the proposed formation of 2-monochlorothiophenoxy radical from molecular 2-monochlorothiophenol. The dissociation energies were calculated at B3LYP/6-31+(d,p) level of theory using DFT. Clearly, such processes proceed with absorption of heat and thus the processes are endothermic. For instance the scission of the phenyl C-OH (scheme 1) proceeds with a high endothermic energy barrier in order to reach the 2-monochlorobenzyl radical. Therefore this pathway is not thermodynamically feasible and will not be discussed further. On the other hand

the formation of 2-monochlorobenzyl radical from the scission of C-SH (scheme 2) takes place with a low energy barrier of 79.60 kcal/mol. This shows that the C-SH linkage in 2-monochlorothiophenol is much weaker than the C-OH linkage in 2-monochlorophenol. This is expected because oxygen is highly electro-negative than sulphur. Nonetheless, the bond dissociation energy of 2-monochlorophenol and 2-monochlorothiophenol to form their respective phenoxy radicals proceed with low energy barriers hence these pathways are biologically important, and will be the subject of critical discussion in this study. More interestingly, the formation of 2-monochlorophenoxy radical takes place with an energy barrier of ~ 85 kcal/mol. As reported in literature (Khachatryan *et al.*, 2008), phenoxy radical formed from unsubstituted phenol proceeds with an energy barrier of $\sim 86 - 87$ kcal/mol. This difference in energy is because of the influence of the Cl substituent on the *ortho* of 2-monochlorothiophenol. Chlorine atom is electron withdrawing hence destabilizes the phenoxy radical and this leads to lowered energy barrier.



Scheme 1: mechanistic channels for the formation of free radicals from 2-monochlorophenol



Scheme 2: mechanistic channels for the formation of free radicals from 2-monochlorothiophenol

The thermochemistry of 2-monochlorophenol and 2-monochlorothiophenol

The change in enthalpy and Gibb's free energies for the formation of free radicals from molecular 2-monochlorothiophenol (Fig. 3A) and 2-monochlorophenol (Fig. 3B) show some interesting relationships. Whereas, the change in Gibb's free energy decreases with increase in temperature, the change in enthalpy increases with increase in temperature for all the species under investigation. Nevertheless, it can be noted that the formation of 2-monochlorothiophenoxy radical from molecular 2-monochlorothiophenol is less endothermic. For instance, at 1000 K enthalpy change for the formation of 2-monochlorothiophenoxy and 2-monochlorophenoxy radicals is 70.40 and 84.39 kcal mol⁻¹ respectively using the 6-31G+(d,p) basis set. The spontaneity of the processes investigated in this work was tested by determining the change in Gibb's free energies. Consequently, the change in Gibb's free energies generally

decreased in the whole range of pyrolysis temperature implying that the reactions presented in schemes 1 and 2 become feasible at high temperatures.

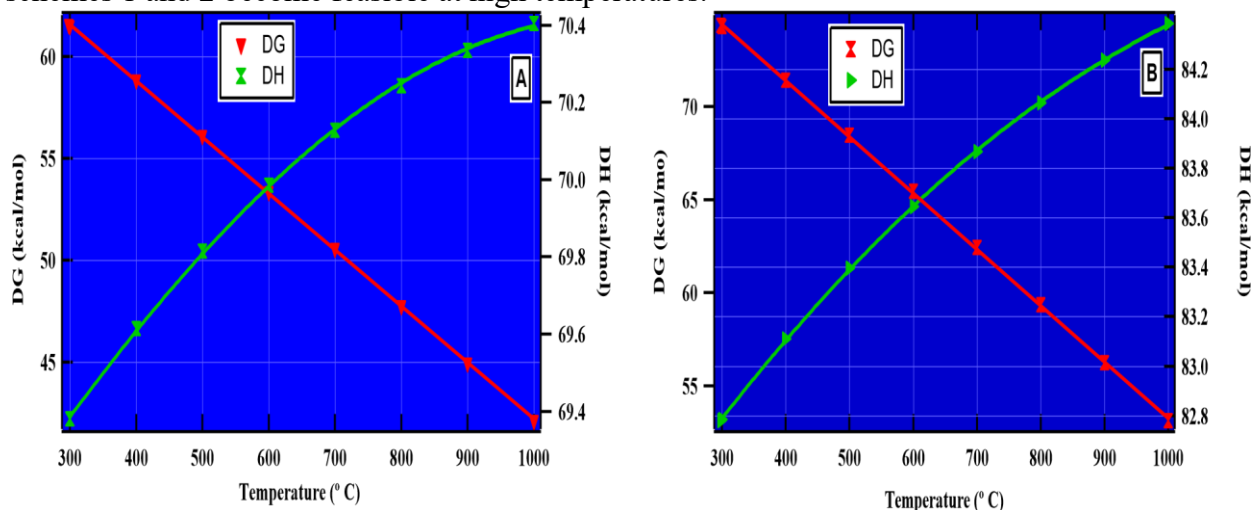


Fig. 3: Plots of thermodynamic parameters (ΔH and ΔG) as a function of temperature for 2-monochlorothiophenol (A) and 2-monochlorophenol (B).

Geometry optimization

The fundamental objective of geometry optimization focuses on the structure with the minimum energy, optimum bond lengths and bond angles. Geometry optimization aims at finding the minimum of a function of numerous variables by ensuring all vibrational frequencies are real. The minima on potential energy surface are critical because they match the optimum geometries of a species as found in its natural form. Thus the geometry of such a structure can be used in a variety of theoretical and experimental investigations such as chemical kinetics, spectroscopy, and thermodynamics. In this work, the geometry optimization and energy calculations were performed quantum mechanically using Gaussian 03 suite using the density functional theory at B3LYP/6-31G+(d,p) correlation function and the results obtained presented in Fig. 4, *vide infra*. Bond lengths are in Angstrom units (10^{-10} m) and the angles are given in degrees. From the data presented in Fig. 3, 2-monochlorophenol has C-Cl bond length of 1.70×10^{-10} m in the input structure while the optimized structure has 1.82×10^{-10} m. The bond angle between atoms hydrogen-oxygen-carbon was 109.5° before the structure was optimized but after optimization the bond angle was found to 111.905° (1C, 11O, 12H). These changes contribute significant differences in both physical and chemical properties. Figs. 4 and 5 give the optimized structures of 2-monochlorophenol and 2-monochlorothiophenol and their corresponding optimization step numbers. 2-MCP takes 7 optimization steps to reach its global minima while 2-MCTP takes optimization steps to be localized. This is expected since 2-MCTP has a higher molecular weight than 2-MCP and probably has a different geometry. The red circle is the optimization level (Figs. 4 and 5, optimization curves).

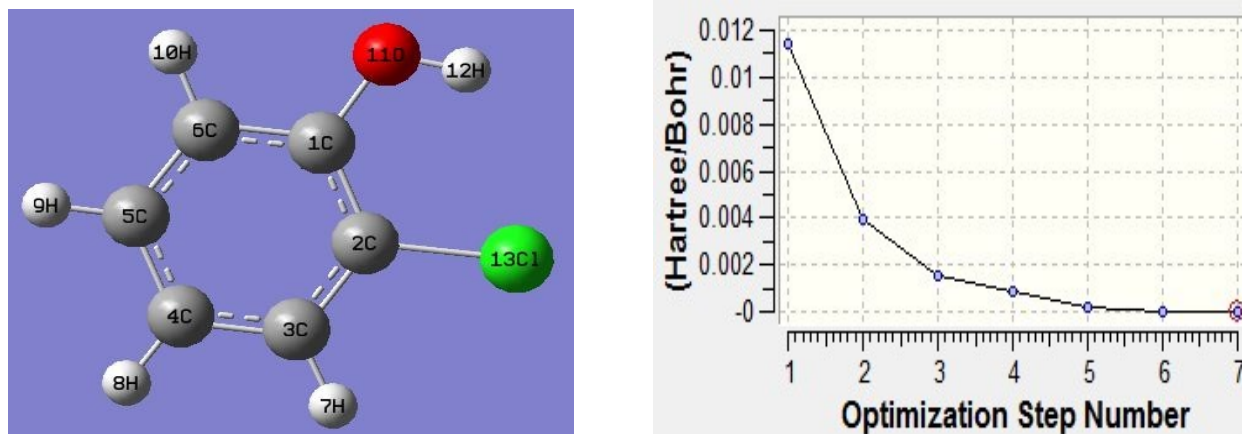


Fig. 4: Optimized structure of 2-monochlorophenol (left) and the optimization step number (right)

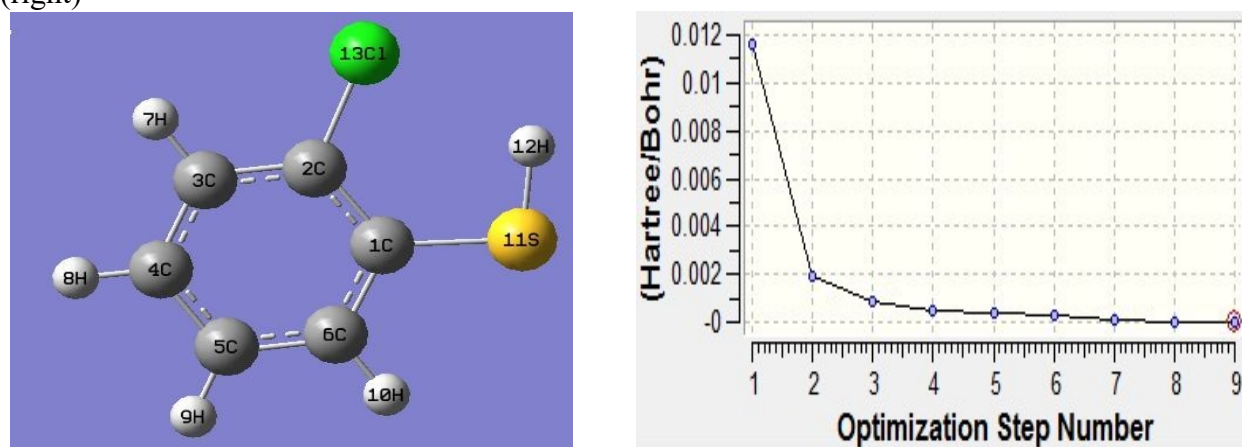


Fig. 5: Optimized structure of 2-monochlorothiophenol (left) and the optimization step number (right)

Molecular orbitals and electronic properties

HOMO- LUMO are well known acronyms for the highest occupied molecular orbital and lowest unoccupied molecular orbital respectively. Fig. 6 gives the molecular orbitals profile for the species investigated in this work at 0.2 isovalue. Chemisian computational framework in conjunction with Gaussian computational code facilitated the calculation of molecular orbitals presented in Fig. 6 (Dar *et al.*, 2012). The energies of the HOMO and LUMO are associated with the most popular quantum-chemical descriptors. The energy difference between the HOMO and LUMO is conventionally termed as the HOMO-LUMO band-gap. HOMO and LUMO orbital energies are related to ionization potential and electron affinity and the respective frontier orbitals are associated with the molecules reactivity i.e. HOMO energy is susceptible to electrophilic attack (donate electrons) and LUMO energy is susceptible to nucleophilic attack (accept electrons). 2-monochlorothiophenol has a lower HOMO energy value of -6.869 eV as compared to 2-monochlorophenol which is energetically higher with its HOMO energy being 6.515 eV indicating that 2-monochlorothiophenol is much more stable than 2-monochlorophenol and hence a good nucleophile.

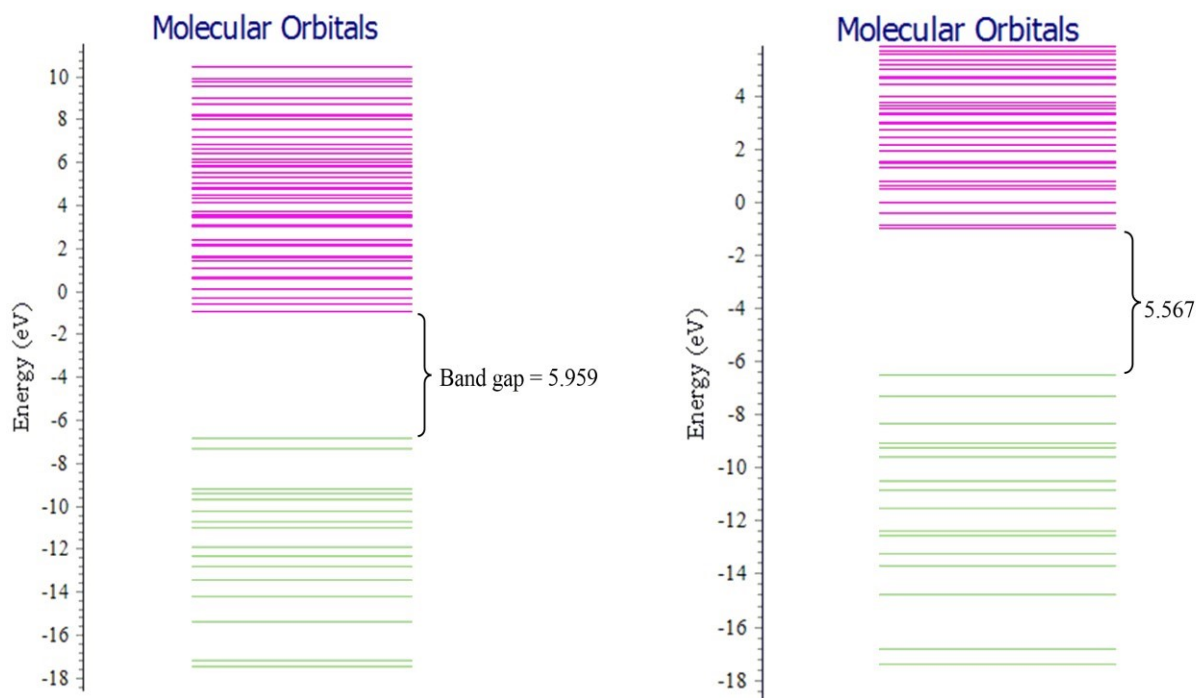


Fig. 6: Orbital profiles for 2-monochlorophenol (left) and 2-monochlorothiophenol (right).

These orbitals determine the chemical reactivity of a compound and the possible mechanism of a chemical reaction. The reactivity index (band gap) of the compounds with small difference implies high reactivity and a large difference implies low reactivity in reactions, therefore as the energy gap between the HOMO and LUMO becomes smaller the reaction rate is favoured.

2-monochlorothiophenol has the smallest HOMO-LUMO energy gap (5.567 eV) and therefore light of enough frequency absorbed by an electron can excite an electron from HOMO to LUMO much more easily. This energy permits electron transfer making 2-monochlorothiophenol highly reactive as compared to 2-monochlorophenol. This observation is attributed to the fact that 2-monochlorophenol has a high band gap energy of 5.959 eV and therefore less reactive.

Electron density maps

Electrostatic potential maps enable us to visualize the charge distribution of molecules and charge related properties of molecules. In the electrostatic maps shown in Figs. 7-8, the electrostatic potential energies of varying positions on the isosurface of the molecules and radical in this study are presented. One of the main purposes of finding the electrostatic potentials is to locate the reactive site of a molecule which has an affinity for interacting with charged particles. The density maps below are coloured according to electrostatic potentials in the Van der Waal's surface. Electron density maps are a useful descriptor for understanding electrophilic and nucleophilic sites. Conventionally, the negative potential sites (red colour) represents regions of electrophilic reactivity and interactions through π - π bonding within aromatic systems and positive potential sites (blue colour) represents regions of nucleophilic reactivity.

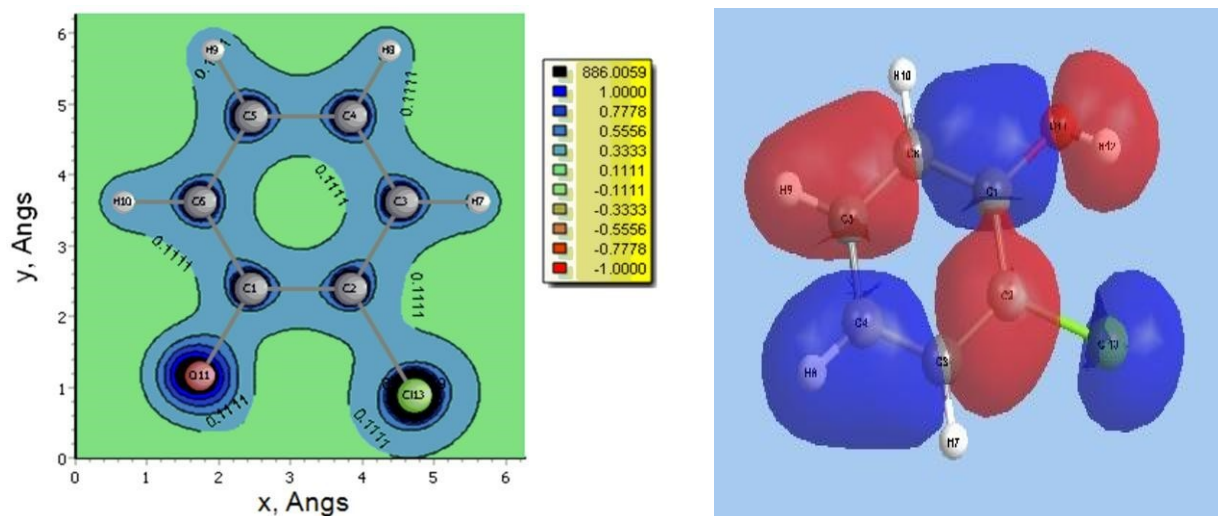


Fig. 7: Electron contour maps and 3-D electron density distribution for 2-monochlorophenol

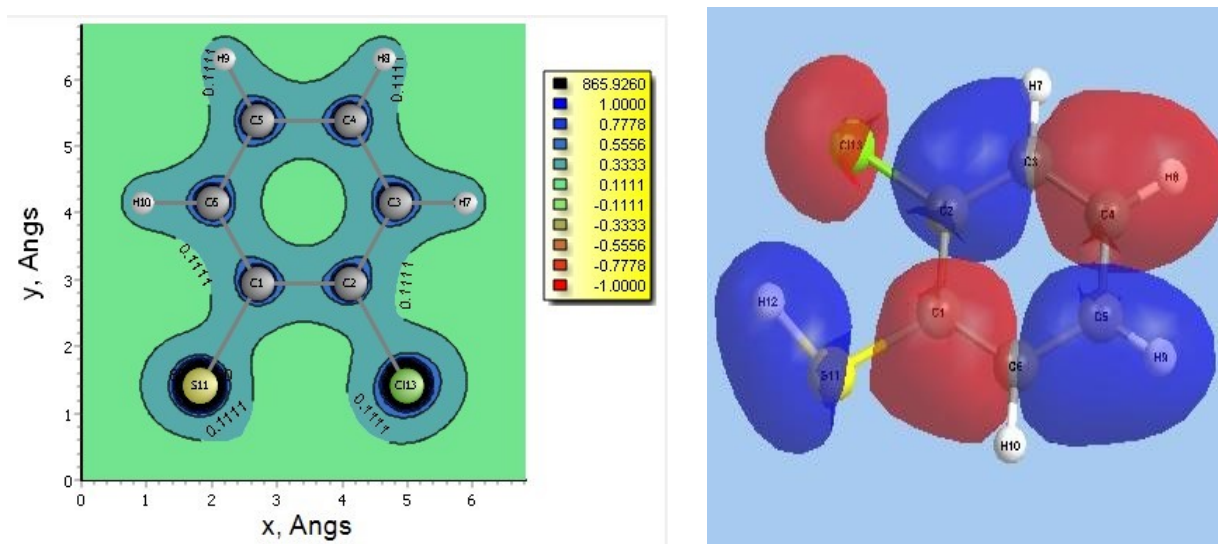


Fig. 8: Electron contour maps and 3-D electron density distribution for 2-monochlorophenol

Areas of low potential have an abundance of electrons. For the 2-monochlorothiophenol molecule and its radical, sulfur has a higher electronegativity value than the other atoms. Thus it has a higher electron density around it than carbon and hydrogen. This is indicated by the deep red colour around its surface. For 2-monochlorophenoxy radical, oxygen has a higher electronegativity than the other atoms (C and H), thus, the higher electron density around its surface. Generally, red indicates the lowest electrostatic potential energy and blue indicates the highest electrostatic potential energy (Figs. 7 -8 *vide supra*).

Toxicity indices

Toxicity indices were calculated using HyperChem computational platform. It uses quantitative structural activity relationship (QSAR) to determine relative toxicity values of a compound and determine its toxicological impacts. Hydration energies provide important information in determining the relative ionic mobilities of a compound. The higher the hydration energy the

higher the solubility of the compound in biological fluids and this may be injurious to body cells. For instance, 2-monochlorophenol has a high negative hydration energy (-8.45 kcal/mol) and thus more reactive. Logarithm of octanol-water partition coefficient is a measure of toxicity and it is an important parameter which significantly affects metabolism and biological functioning of the body system (Debnath, 1994; Hansch *et al.*, 1991; Smith & Hansch, 2000).

Table 1: QSAR properties for the components investigated in this study

Compound/radical	$\log P$	P	Hydration energy (kcal/mol)	Surface Area ($\text{\AA}^2$)	RMM (g/mol)
2-monochlorothiophenol	0.59	3.89	- 3.55	331.61	123.52
2-monochlorothionyl radical	0.49	3.09	-3.38	273.71	164.01
2-monochlorophenol	0.35	2.24	-8.45	303.15	163.00
2-monochlorophenoxy radical	1.77	58.88	-3.36	261.55	143.61

From the results in table 1, the value of Log P for 2-monochlorophenol is 0.35 and was noted to be lower than that of 2-monochlorothiophenol which has a value of 0.59. This suggests that 2-monochlorophenol is more soluble in water than in octanol because of its polarity. This polar nature suggests that it can react with polar biological compounds to initiate oxidative stress and ultimately cancer and trigger reactive oxygen species (ROS). More interestingly, 2-monochlorophenoxy radical is more soluble in octanol than water implying that it is highly hydrophobic and may possibly react with non-polar biological compounds such as lipids which may also lead to cell aberrations and mutation. Generally, these compounds can cause serious health impacts in high order animals including man and natural ecosystems.

Conclusion

This contribution has revealed that the transformation of 2-monochlorothiophenol to its corresponding free radical (2-monochlorothiophenoxy radical) is less endothermic than the formation of 2-monochlorophenoxy radical from molecular 2-monochlorophenol. This implies that 2-monochlorothiophenol easily forms environmentally free radicals in combustion systems such as municipal waste incineration, tobacco smoke, and forest fires. Nevertheless, 2-monochlorophenoxy radical is expected to be more reactive because oxygen is highly electronegative reactive than sulphur and may therefore be more injurious in biological systems than the sulphur based 2-monochlorothiophenoxy radical. The presence of chlorine substituent destabilizes the radical because it is electron withdrawing. Thus the energy barrier during the formation of the corresponding phenoxy radical is lowered. Additionally, the toxicity values indicate that molecular 2-monochlorophenol is polar and thus can react with polar biological fluids causing serious health problems. Nonetheless, its corresponding free radical is less polar but can cross hydrophobic barriers in biological systems such as skin stratum and lipids to cause oxidative stress and growth of tumors. Molecular orbital profiles calculated using Chemission showed that 2-monochlorothiophenol is significantly nucleophilic whereas 2-monochlorophenol is electrophilic.

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References

- Abhilash, P. C., & Singh, N. (2008). Distribution of Hexachlorocyclohexane Isomers in Soil Samples From a Small Scale Industrial Area of Lucknow, North India, Associated With Lindane Production. *Chemosphere*, **73**(6), 1011-1015.
- Acros. (2015). *Safety Data Sheet*.
- Adane, B., Khalid, S., & Nathan, M. (2015). Kinetic, Equilibrium and Thermodynamic Study Of 2-Chlorophenol Adsorption Onto Ricinus Communis Pericarp Activated Carbon From Aqueous Solutions. *Green Chemistry Letters and Reviews*, **8**(3), 1-12.
- Ajeel, M. A., Aroua, M. K., & Daud, A. W. (2015). Anodic Degradation of 2-Chlorophenol by Carbon Black Diamond and Activated Carbon Composite Electrodes. *Electrochimica Acta*, **180**, 22-28.
- Ames, B. N., Cross, C. E., Halliwell, B., Borish, E. T., Pryor, W. A., Saul, R. L., & Harman, D. (1987). Oxygen Radicals and Human Diseases. *Annals of Internal Medicine*, **107**(4), 526-545.
- Baleke, G. U., Wegener, S., Kiesel, B., Benndorf, D., Schlömann, M., & Vogt, C. (2008). Kinetics of chlorobenzene biodegradation under reduced oxygen levels. *Biodegradation*, **19**(4), 507-519.
- Becke, A. D. (1993). Density functional thermochemistry. III. The role of exact exchange. *The Journal of chemical physics*, **98**(7), 5648-5652.
- Boyd, E., Killham, K., & Meharg, A. (2001). Toxicity of mono-, di- and tri-chlorophenols to lux marked terrestrial bacteria Burkholderia species Rasc C2 and Pseudomonas fluorescens. *microbiol. Let.*, **43**, 157.
- Cheng, Y., Lu, S., Zhang, H., Varanasi, C. V., & Liu, J. (2012). Synergistic effects from graphene and carbon nanotubes enable flexible and robust electrodes for high performance supercapacitors. *Nano letters*, **12**(8), 4206-4211.
- Cooper Sr, A. R. (1996). *Cooper's toxic exposures desk reference with CD-ROM*: CRC Press.
- Dar, T., Altarawneh, M., & Dlugogorski, B. Z. (2012). Theoretical study in the dimerisation of 2-chlorothiophenol/2-chlorothiophenoxy: Precursors to PCDT/TA. *Organohalogen Compounds*, **74**, 657-660.
- Daraei, H., & Kamali, H. (2014). Experimental Design and Response Surface Modeling for Optimization of 2-Chlorophenol Removal from Water by Nanoscale Iron and Fe Powder. *Journal of Environmental & Analytical Toxicology*, **4**, 228.
- Dayan, A. D. (1993). Carcinogenicity and drinking water. *Pharmacology & toxicology*, **72**(s1), 108-115.
- Debnath, A. K., Shusterman, A. J., deCompadre, R. R. L., Hansch C. (1994). Importance of the hydrophobic interaction in the mutagenicity of organic compounds. *Mutation Research*, **305**, 63-72.
- Fei, X., Xiangli, S., Yunfeng, L., & Qingzhu, Z. (2015). Mechanistic and Kinetic Studies on the Homogeneous Gas-Phase Formation of PCTA/DTs from 2,4-Dichlorothiophenol and 2,4,6-Trichlorothiophenol. *Int. J. Mol. Sci*, **16**(9), 20449-20467.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., . . .

- Burant, J. (2004). Gaussian 03, revision c. 02; Gaussian. Inc., Wallingford, CT, 4.
- Gonzalez, M. A., Texier, A. C., Lartundo, L. C., & Gonzalez, I. (2015). Electrochemical Dechlorination of 2-Chlorophenol on Pd/Ti, Ni/Ti and Pd-Ni Alloy/Ti Electrodes. *Journal of Electrochemical Society*, **162**(10), 223-230.
- Hansch, C., Leo, A., & Taft, R. W. (1991). A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chemical Reviews*, **91**(2), 165-195.
- Igbinsola, E. O., Odajadjare, E. O., Chigor, V. N., Isoken, H. I., Emoghene, A. I., Ekhaize, F. O., . . . Idemudia, O. G. (2013). Toxicological Profile of Chlorophenols and Their Derivatives in the Environment: The Public Health Perspective. *Scientific World Journal*, **2013**(2013), 11.
- Jin, J., Liu, B., Yang, B., Gan, Y., & Bao, C. (2016). Electrochemical Analysis of 2-chlorophenol Using a Multi-Walled Carbon Nanotube-Ionic Liquid Composite Modified Electrode. *Int. J. Electrochem. Sci.*, **11**, 3931-3937.
- Joseph, C. G., Liew, Y. L., Krishnaiah, D., & Bono, A. (2012). Application of a Semiconductor Oxide-Based Catalyst in Heterogeneous Waste Water Treatment: A green technology Approach. *Journal of Applied Sciences*, **12**(18), 1966-1971.
- Khachatryan, L., Adoukpe, J., and Dellinger, B. (2008). Formation of Phenoxy and cyclopentadienyl radicals from the gas-phase pyrolysis of phenol. *J.Phys.Chem., A*, **112**, 481-487.
- Koumanova, B., P., P.-A., & Yaneva, Z. (2005). Adsorption of 4-chlorophenol from aqueous solutions on activated carbon-kinetic. *Stud. J Uni Chem Tech Metal*, **40**, 213-218.
- Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B*, **37**(2), 785.
- Leonid, S. (2012). Chemissian (Version 3.3): Chemissian. Retrieved from <http://www.chemissian.com/>
- Mahammad, M. A., Alireza, M., & Shima, R. (2015). Evaluation of Removal Efficiency of 2Chlorophenol in Aquatic Environments by Modified Fly Ash. *Environmental Health Engineering and Management Journal*, **2**(4), 179-185.
- Michałowicz, J., & Duda, W. (2007). Phenols- sources and toxicity. *Polish J. of Environ. Stud.*, **16**(3), 347-362.
- Muneer, M. B., Abdul, A. H., Ahmed, A. A., Abu Bakar, M., & Mohd, S. T. (2012). Toxicity Evaluation For Low Concentration Of Chlorophenols Under Solar Radiation Using Zinc Oxide (Zno)Nanoparticles. *International Journal of the Physical Sciences*, **7**(1), 48-52.
- Navarro, R., Bierbrauer, K., Mijangos, C., Goiti, E., & Reinecke, H. (2008). Modification of Poly(vinylchloride) With New Aromatic Thiol Compounds. Synthesis and Characterization. *Polym. Degrad. Stab*, **93**, 585-591.
- Ochterski, J. W. (2000). Thermochemistry in gaussian. *Gaussian Inc*, 1-19.
- Ohashi, Y., Yamada, K., Takemoto, I., Mizutani, T., & Saeki, K. (2005). Inhibition Of Human Cytochrome P450 2e1 By Halogenated Anilines, Phenols, And Thiophenols. *Biol. Pharm. Bull.*, **28**, 1221-1223.
- Parette, R., & Pearson, W. N. (2014). 2,4,6,8-Tetrachlorodibenzothiophene in the Newark Bay Estuary: The likely source and reaction pathways. *Chemosphere*, **111**, 157-163.
- Shi, J. Q., Cheng, J., Wanga, F. Y., Flamm, A., Wang, Z. Y., Yang, X., & Gao, S. X. (2012). Acute Toxicity And N-Octanol/Water Partition Coefficients Of Substituted Thiophenols: Determination and QSAR Analysis. *Ecotoxicol. Environ. Saf.*, **78**, 134-141.

- Shokufeh, A., Bahram, K., & Ali, J. (2016). 2- Chlorophenol Removal of Aqueous Solution Using Advanced Oxidation Processes Resulting from Iron/ Persulfate and Ultra Violet/ Persulfate. *Iranian Journal of Toxicology*, **10**(4), 1-8.
- Smith, C. J., & Hansch, C. (2000). The relative toxicity of compounds in mainstream cigarette smoke condensate. *Food and Chemical Toxicology*, **38**(7), 637-646.
- Sullivan, M. J., Ladd, D. A., Bulpitt, D. A., & Comeau, B. (2008). Rubber compositions comprising high levels of oily substance and the use thereof in golf balls: Google Patents.
- Wójcik, J., Peszke, J., Ratuszna, A., Kuś, P., & Wrzalik, R. (2013). Theoretical investigation of porphyrin-based photosensitizers with enhanced NIR absorption. *Physical Chemistry Chemical Physics*, **15**(45), 19651-19658.