

REVIEW OF CHLOROPICRIN A FUMIGANT ANOTHER ENVIRONMENTAL POLLUTANT

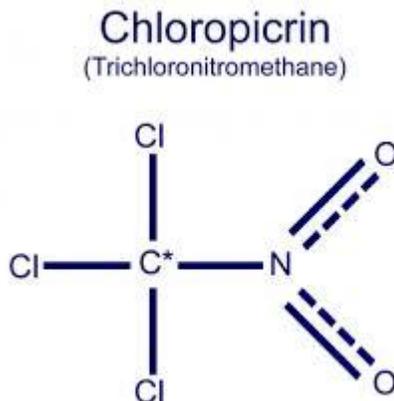
Jyoti Kumari¹

Abstract-Chloropicrin is a chemical compound used to kill fungi, nematodes, microbes present in soil. Thereby it increases the productivity in agriculture. Chloropicrin is useful but it is harmful like other pesticides (DDT) because it acts as a pollutant. Its emission in environment increases the pollution level in air. In This article we discuss properties of chloropicrin and its relation with formation of ozone, a pollutant in troposphere.

Keywords-Herbicide, Pollution, Troposphere, Photolysis, Free-radical, Experiment chamber, Organic compounds.

1. INTRODUCTION

Chloropicrin is also known as trichloro nitro methane whose structure can be written as



Chloropicrin is a chemical compound currently used as abroad spectrum antimicrobial, fungicide and herbicide. Initially it has been used as chemical weapon agent during world war. Chloropicrin is used as a reagent in the synthesis of organic chemicals, in the manufacture of methyl violet, and as a fumigant, it has also been used in chemical warfare agent. it is used as tear gas due its strong irritating nature. Sometime it is used as warning agent for fumigant methyl bromide and hydrogen cyanide (HCN).

2. PROPERTIES OF CHLOROPICRIN

1. Chloropicrin is highly volatile and due to this property it becomes a source of air pollution.
2. It acts as a powerful tear gas.
3. It has a strong odour so it is used as a warning agent when added in small amount to other fumigants such as HCN and CH₃Br.
4. It is soluble in acetic acid, organic solvents, phosgene and alcohol.
5. It is non combustible agent but on heating it may decompose to produce irritating and toxic gases.
6. Liquid chloropicrin will attack some form of rubber.
7. It is chemically inert but it can attack iron, zinc and some light metals.
8. Decomposition of chloropicrin may release nitrogen oxides, phosgene, nitrosyl chloride, chlorine and carbonyl.
9. On contact with metals, it may produce hydrogen gas.
10. It is non inflammable but its reaction with oxidizing agent produce fire or explosion.
11. It is stable in cold, dilute aqueous NaOH but slowly decomposes in ethanolic KOH. It undergoes more rapid decomposition with sodium ethoxide or ethanolic sodium cyanide.

¹ Kurukshetra University, Kurukshetra (Haryana), India

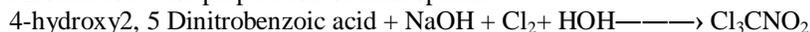
12. Solution of chloropicrin in acetone decomposes slowly and deposits ammonium chloride.
13. Chloropicrin on slow thermolysis under reflux produce phosgene and nitrosyl chloride
14. OR
15. Chloropicrin+20% Fuming Sulphuric acid ----decomposition-----= NOCl +Phosgene.
16. It is dehalogenated with aqueous sulphite (SO_3^{2-}) to form dichloronitromethane(CHCl_2NO_2).
17. Chloropicrin reacts with iodide to form carbon tetraiodide.
18. Chloropicrin reacts with iron bearing clay minerals to produce both chloronitromethane and dichloronitromethane.
19. It can be used to prepare orthocarbonates, $\text{C}(\text{OR})_4$, the process involving four replacements by alkoxide ion.
20. Chloropicrin is reduced to chloroform when reducing agents are added to remove excess chlorine in water. In the presence of light, it is degraded to carbon dioxide, chloride ion and nitrate ion.

3. PREPARATION

It can be prepared by reacting picric acid and NaOCl



Another route for preparation of chloropicrin



4. EFFECT OF CHLOROPICRIN ON ENVIRONMENT

Chloropicrin does not accumulate in soil or water due to its highly volatile nature. It gets evaporated in air that is termed as chloropicrin emission. It may be during transport. Use or handling, ultimately chloropicrin reaches to atmosphere. It is studied that this pesticide is very toxic to humans, animals, aquatic life, fungi, nematodes and microbes. So user should be more cautious while using this pesticide to avoid its discharge into lakes, streams, pond and oceans. Chloropicrin is extensively used as preplant soil fumigant in agriculture due to its volatile nature, it affects atmosphere that surround us. Therefore it is sufficiently reactive and it may stimulate the formation of tropospheric ozone which is a major pollutant in troposphere. Chloropicrin reacts in same way as other volatile organic compound reacts with free radicals present in atmosphere. It may react with hydroxide radical, NO radical or with ozone or undergo direct photolysis, this chloropicrin behaves like other organic compound and reaction occurs via free radical.

Moilanen et al (1978) studied the photolysis of chloropicrin in presence of oxygen.

Mode1.

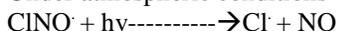


Other route of photolysis can be

Mode2

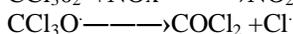
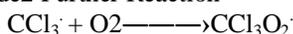


Under atmospheric conditions CINO Radical undergo further reaction.



This chlorine radical starts further reaction of formation of ozone via number of free radical intermediate.

Mode2 Further Reaction



This chlorine radical enhance the overall level of radicals in atmosphere, this radical will start further reaction of ozone formation. This is experimentally studied in environmental chamber experiment however, free radical chlorine does not start direct reaction of ozone formation but can indirectly cause ozone formation and in most cases it generate hydroxide radical which will start further reaction with volatile organic compound which produce ozone in tropospheric layer of atmosphere. In environmental chamber experiment, chloropicrin enhanced rate of NO oxidation ozone formation and consumption of alkane and other organic reactants. This is attributed to formation chlorine radical and NOx in its decomposition. Ozone production continues as long as sufficient NOx is present.

Chloropicrin increase pollutant level in atmosphere and this increased pollution lead to formation of smog that is called as photochemical smog. Ozone is protective layer around in stratospheric layer of atmosphere that protect us from harmful UV radiation of sun but its formation in troposphere is considered as pollutant because ozone participates in reactions of smog formation.

5. EFFECT ON PLANT LIFE

Chloropicrin is extremely toxic and plants exposed directly to its vapours are often completely destroyed.

6. EFFECT ON HUMAN LIFE

It is very toxic to human life. It is a powerful irritating compound affecting all body parts. It is used as tear gas to control riots. It affects respiratory organs thus it is known to be a lung damaging agent.

7. CONCLUSION

Chloropicrin is widely used in agriculture because of its special property of killing pest but its increasing use poses a new threat to human, animals and plants life. Chloropicrin emission in atmosphere acts as a precursor of ozone in indirect way. So its use should be checked. Chloropicrin may induce smog formation due to free radical reaction of chlorine, so other alternative with more safety should be discovered and more research should be done to investigate proper mechanism of reaction of chloropicrin.

8. REFERENCES

- [1] Content source-national institute for occupational safety and health (NIOSH) education. Information division; www.cdc.gov.in
- [2] Meister, R. T. (1995) Farm chemical handbook 195. Meister publishing company. Willoughby 12:673-681.
- [3] Yoshida M. et al. (1987). Subchronic inhalation toxicity of chloropicrin vapours in rats. *T. Pesticides Sci.*
- [4] Handbook of environmental data on organic chemicals. 1983. Verschuere publishing Co. p.384
- [5] Moilanen, K. W. D. G. Crosby and J. Humphrey 1978. Vapour phase photodecomposition of chloropicrin tetrahedron. 34. pp.3345-3349.
- [6] U. S. Environmental Protection Agency. 1992. Pesticide Environmental Fate One Line Summary: Chloropicrin. USEPA Environmental fate and effects division, Washington.
- [7] Tomlin (2004-05) CDS, ed. Chloropicrin (76-06-2). In: The e-pesticide manual. 13th edition version 3.1 Surrey UK, British crop protection Council.
- [8] Pearson C.R. et al. (2005) *Environ Toxicol Chem* 24:3037-42.
- [9] Moilanen, K.W., D.G CROSBY, J.R Humphrey and J. W. Giles (1978): vapour phase decomposition of chloropicrin, *tetrahedron*, 34. 2245-3349.
- [10] Atkinson, R. (1990): "gas phase tropospheric chemistry of organic compounds: A Review," *Atmos. Environ.*, 24A, 1-24.
- [11] William P. L. Carter, Dongmin Luo and L. Malkina (1996): investigation of the atmospheric reactions of chloropicrin.
- [12] Atkinson, R (1994) Gas phase tropospheric chemistry of organic compounds," *J. Phys. Chem. Ref. Data*
- [13] Carter, W. P. L. (1994): Development of ozone reactivity scales for volatile organic compounds, *J. Air and waste manage. Assoc.*, 44, 881-899.
- [14] Careter. W. P. L. D. Luo, I. L. Malkina, and J.A. Pierce (1995): Environmental chamber studies of atmospheric reactivities of volatile organic compounds.
- [15] Zafonte, L., P. L. Rieger and J.R. Holmes (1997): Nitrogen dioxide photolysis in the Los Angeles Atmosphere, *Environ. Sci. Technol.* 11. 483-487.
- [16] P. Howard, (1990) Handbook of Environmental fate and exposure data for organic chemistry (1990) 126.
- [17] Elisabeth A. Wade, Krishna E. Reak, Bradley F. Parsons, Thomas P. Clemes, Karen A. Singmaster (2002): photochemistry of chloropicrin in cryogenic matrices 365(2002)473-479.
- [18] J. Gan, S. R. Yates, F. F. Ernst and W. A. Jury. CA 92507-92521: "Degradation and volatilization of the fumigant chloropicrin after soil treatment.
- [19] WILHEM, S. N., K. Shepler, L. J. Lawrance, and H. Lee. 1997. Environmental fate of chloropicrin. 79-93. In J.N. Seiber et al. (ed) *Fumigants: environmental fate, exposure and analysis.* ACS Symp. Ser. 652. ACS, WASHINGTON
- [20] Department of Pesticide Regulation California Environmental Protection Agency (2010): EVALUATION OF CHLOROPICRIN AS A TOXIC AIR CONTAMINANT.