

Formation of Toxic Species in Thermal Decomposition of Captan

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Abstract

Captan belongs to an important group of sulfenimide fungicides, commonly used on major crops, fruits and ornamentals. In this study, a laboratory scale apparatus has been constructed to investigate the thermal decomposition of captan in gas phase reactions, similar to those that occur in fires, burning of wood and other biomass treated or contaminated with pesticides. The apparatus comprises a plug flow reactor equipped with sampling systems for gaseous, volatile and condensable products. The gaseous species were detected and quantified by the Fourier transform infra-red spectroscopy (FTIR). The volatile organic compounds (VOC) were trapped in an activated charcoal tube and the condensable products were collected by XAD resin and cold solvent traps. The identification of VOC was performed by means of high resolution gas chromatography–quadrupole mass spectrometry (HRGC-QMS). Under oxidative atmosphere, the thermal decomposition of captan generated gaseous pollutants including carbonyl sulfide, carbon disulfide, thiophosgene and phosgene (the World War I chemical agent). The VOC analysis revealed the formation of tetrachloroethylene, hexachloroethane (both suspect carcinogens) and chlorinated benzenes. At higher temperature, the decomposition of captan vapour produced, mono to tetra, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), with PCDD/F quantified on an HRGC-MS/MS (ion trap) instrument.

Keywords: Captan, Combustion, Air pollutants, PCDD/F.

1. Introduction

Captan is a nonspecific sulfenimide fungicide. It is applied to control diseases of vegetable crops, fruits and ornamentals [1]. Introduced in the early 1950s, it now ranks as the second most abundant fungicide in apple and peach orchards in the USA [2]. In California alone, the statistics show 215,301 acres treated with captan in 2007 [3]. Captan is also widely employed in industries such as cosmetics, paints, and textiles [4].

Worldwide, the severe consequences of accidental chemical fires in storage facilities and widespread burning of pesticide treated biomass reinforce the need for better understanding of combustion processes involving pesticides [5, 6]. The presence of sulfur and relatively high content of chlorine (35.4%) in captan may lead to emissions of toxic sulfides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in combustion processes [7].

Unfortunately, there have been surprisingly few detailed studies on captan combustion. Although toxic gases were detected when captan was heated to 400 – 425 °C [8], the absence of gas product quantification and no analyses of volatile organic compounds (VOC) and condensed products enables no quantitative risk evaluation nor the investigation of decomposition pathways. A study on the thermal decomposition of captan should be useful in assessing the impact of its combustion on the environment. For this reason, in the present work we investigate the thermal decomposition of captan vapour at 400 and 600 °C in oxygen containing atmosphere to determine the formation of toxic species. The lower temperature was selected to gain an understanding of unimolecular initiation reactions, whereas the higher to elucidate the bimolecular reactions.

2. Experimental Setup

The experimental setup consists of three sections: a pesticide vaporiser, an alumina tubular-flow reactor and product collection systems. Figure 1 illustrates the three sections each drawn in a distinct colour.

Pesticide vaporiser: Captan (98%, TCI, Japan), a white solid powder at room temperature, was placed in an polytetrafluoroethylene (PTFE) tube of 8 mm inner diameter (i.d.), vertically installed in a GC oven (Shimadzu, Japan). The oven heated up to 150 °C, slowly generating captan vapour (approximate 0.045 mg/min). Then the vapour was diluted in nitrogen flow and mixed with a controlled amount of oxygen prior to entering the reactor. The concentration of O₂ was monitored on the molecular sieve 5A channel of a CP2003 micro gas chromatography (Varian, USA).

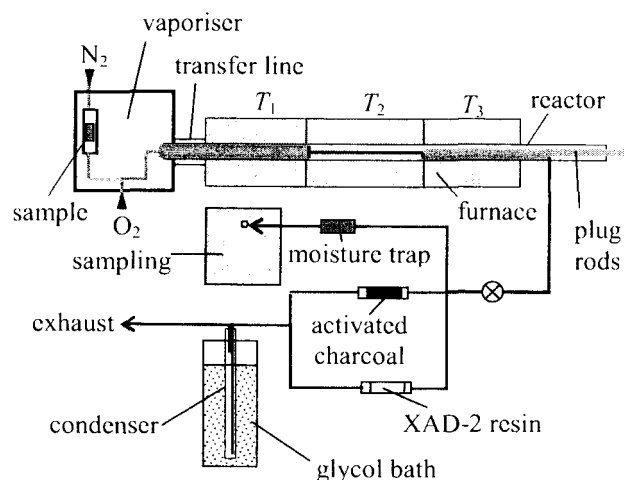


Fig.1 Schematic of the experimental set-up

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Reactor: The reactor section is an alumina tube (99.8 %) with i.d. of 5 mm, aligned along the centreline of a three-zone furnace. Each zone can be configured independently (Eurotherm 3216, Australia). The furnace has been calibrated up to 600 °C with a thermocouple placed along the tube to define the location of a uniform temperature zone (24 cm). Two smaller alumina rods with outside diameter of 4 mm were plugged in both ends of the reactor for two purposes: (1) to ensure that the vapour reaches the reaction zone rapidly, minimising decomposition in lower temperature regions; (2) to maintain the same residence time at different temperature, by changing the inserted length of the rod at the back end to adjust the length of reaction zone. To connect the front of reactor with the adjacent pesticide vaporiser, a transfer line was maintained at 175 °C with a coiled tubular heater (Helios, Australia), to prevent captan vapour from condensing prior to the reactor. The other end was attached to different product collection systems.

Product collection systems: The sampling time from the reactor was set at one hour for each run. The connection tubes, made of PTFE, were cleaned with methanol/acetone solution, to remove adsorbed products and to avoid contamination of subsequent runs [9]. The gaseous species were dried by passing them through a desiccant tube and collected in a sampling bag for the FTIR spectroscopic analysis. A glass tube with 100 mg activated charcoal (Merck, Australia) functioned as a VOC trap. As absorbent for PCDD/F, we loaded 200 mg of XAD-2 resin (Supelpak-2, Sigma-Aldrich, Australia). To conclude the sampling line, a dichloromethane (DCM) and methanol solvent trap was chilled in a cold glycol bath (0 °C).

FTIR analysis: Infrared spectra of gaseous products were recorded on a Varian 660-IR spectrometer (Varian, Australia) equipped with a 10-PA long path gas cell (Infrared Analysis, USA). The evacuated gas cell was firstly filled with sample gas and then brought back to atmospheric pressure by filling with five nines nitrogen; i.e., GC carrier gas grade. We scanned each sample 32 times in the range of 4000-500 cm^{-1} with a resolution of 0.5 cm^{-1} . For the identification of gaseous products, we employed the reference spectra of QASoft software package (Infrared Analysis, USA). These spectra required a correction for slight frequency shifts relative to our samples, owing to a difference in the alignment of optical parts of our instrument with respect to that used to collect the reference spectra. For quantitative analysis of FTIR spectra, we employed the region integration and subtraction routine of the same software. The accuracy of the determination is highly dependent upon that of the reference spectra. The distinct band(s) of the identified compound were selected for integration, with the signal intensity maintained in the linear region; i.e., a true absorbance kept at below 0.7 [10].

GC-MS analysis of VOC: For the identification of VOC, we modified the general procedures of the National Institute for Occupational Safety and Health (NIOSH) Method 1003, as necessary for our

instrument. The CS_2 extract was filtered and injected (split 50) into the Varian CP3800 high resolution gas chromatograph (HRGC) and Varian 1200 quadrupole mass spectrometer (QMS), equipped with a 30 m Varian VF-5ms column (i.d. of 0.25 mm, film thickness of 0.25 μm). While the injector maintained the temperature at 180 °C, the temperature program of the GC oven started at 35 °C, held for 3 min, then imposed a temperature ramp of 10 °C/min up to 180 °C, held for one min, to conclude the heating at 250 °C at a rate of 20 °C/min. MS ionisation electron impact voltage was set at 70 eV and the source maintained at 200 °C. The eluted peaks were identified by matching their mass spectra with those from the NIST library.

GC-MS/MS analysis of PCDD/F: We modified the United States Environmental Protection Agency (USEPA) Standard Method 1613 to include the determination of mono- to tri- chlorinated congeners (refer to Appendix for the details of GC and MS operating parameters). At the end of an experiment, the XAD-2 resin was soxhlet (Buchi Extraction System-B-811) extracted in a hot mode with toluene for 5 hours. The extract and DCM solvents from washing the reactor tube and other sampling parts were concentrated separately. Subsequently, the solutions were cleaned up with glass chromatography columns loaded with acid and basic alumina and concentrated again prior to HRGC-MS/MS (ion trap) analysis.

3. Results and Discussion

The experimental results discussed here were carried out at 400 and 600 °C with a residence time of 1 s under an atmosphere of 6 ± 0.5 % of O_2 in N_2 (v/v).

Figure 2 displays typical spectra collected by FTIR spectrometer, with the water vapour interference removed, for gases captured from the experiment performed at 400 °C. Assisted by the reference spectra of the QASoft package, we identified 11 gaseous species produced at 400 °C, with the absorption bands of product gases indicated in Fig. 2. We also applied the reference spectra to quantify the concentrations of product gasses. Table 1 lists the relevant wavenumber ranges for integration together with the yields of all products reported as mole percentage of initial captan. Since one mole of captan can potentially lead to three moles of HCl, its mole concentration was divided by 3 to calculate the yield. Similarly, the concentrations of

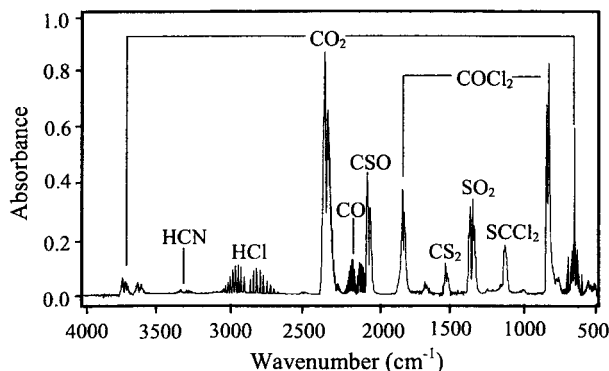


Fig. 2 FTIR spectrum of experiment at 400 °C

carbon oxides were divided by 9 and the concentration of carbon disulfide was multiplied by 2. The results of repeated runs suggest a reasonable reproducibility with the relative standard deviation (RSD) of each product of less than 11%.

Phosgene and thiophosgene (both very toxic) exhibit significant yields at 400 °C and dominate the chlorinated gases. However, their yields descent to zero as temperature increases to 600 °C. Yields of chloroform and carbon disulfide also decrease towards zero with increasing temperature. Yields of the remaining species all show increases as temperature rises from 400 to 600 °C. Gaseous toxic pollutants only form under relatively lower temperatures; i.e., below 600 °C. At higher temperature, the pesticide expectedly oxidizes to oxides of carbon, sulfur and nitrogen.

We detect no unreacted captan and condensed phase products containing chlorine and sulfur, with HCl probably underestimated in FTIR measurements. Possible losses of HCl gas is a consequence of its conversion to hydrochloric acid, owing to the presence of moisture as a product gas, or its adsorption on surfaces such as glass and stainless steel. This suggests that the measurements of HCl reported here correspond to FTIR detectable values. The additional ion chromatographic (IC) analysis of Cl⁻ showed an improved chlorine recovery of 83% at 400 °C. Upon conclusion of the experiments, we observed a yellowish brown residue on the inner surfaces of the reactor tubes at 400 °C while the tubes were clean at 600 °C. The presence of SO₂ in the FTIR spectrum and in the oxidation-product residue indicates that elemental sulfur may form in the captan decomposition. This result explains that the sulfur mass balance observed at 400 °C is less than that at 600 °C (89%).

Figure 3 illustrates the results of the HRGC-QMS analysis of VOC. Among the six major products identified in the chromatograms, hexachloroethane (HCA) is a major species at 400 °C, but not detected at the higher temperature. Tetrachloroethylene (TCE) was unequivocally detected only at 600 °C. The International Agency for Research on Cancer (IARC) classifies both HCA and TCE as suspect carcinogens. Another important decomposition product from the tetrahydrophthalimide moiety in captan molecule,

Table 1. Quantitative results of FTIR analysis

Product	Wavenumber range (cm ⁻¹)	Yield (%)	
		400 °C	600 °C
Hydrogen chloride	2822 - 2821	17	27
Phosgene	1821 - 1788	22	0
Thiophosgene	1151 - 1136	12	0
Chloroform	1225 - 1215	1	0
Carbonyl sulfide	2056 - 2023	14	26
Carbon disulfide	1537 - 1532	5	1
Sulfur dioxide	1363 - 1357	44	62
Carbon monoxide	2174 - 2156	6	10
Carbon dioxide	670 - 666	30	47
Benzene	676 - 672	4	8
Hydrogen cyanide	712 - 710	5	11

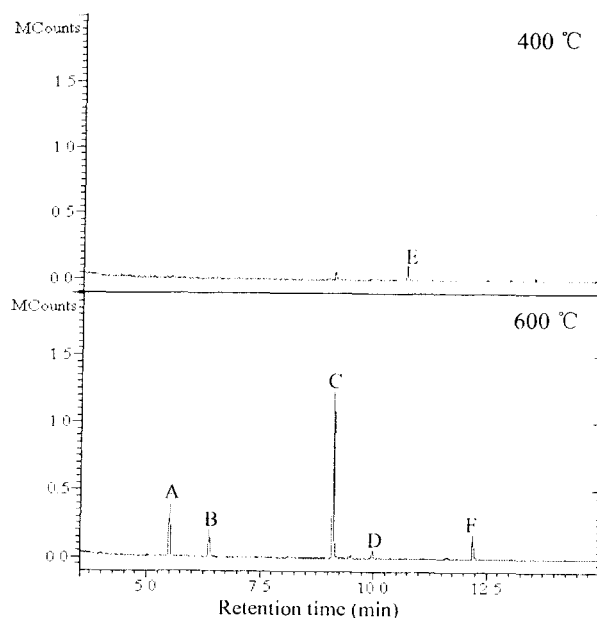


Fig. 3 Chromatograms of VOC analysis: A - tetrachloroethylene; B - chlorobenzene; C - benzonitrile; D - dichlorobenzene; E - hexachloroethane; F - chlorobenzonitrile

benzonitrile, has its signal increasing with temperature from 400 to 600 °C. We have also observed the peaks of chlorobenzene (CB), dichlorobenzene (DCB) and chlorobenzonitrile at 600 °C. No chlorine is directly attached to the cyclohexene ring of captan, thus the presence of these products suggests that free-chlorine radicals react with the aromatic ring in the decomposition processes. A large number of studies support the proposition that CB and DCB act as precursors, leading the formation of PCDD/F under the oxidative conditions [12].

The experiment involving sampling of PCDD/F continued for six hours, compared with one-hour sampling time afforded for experiments described in the previous paragraphs. The detection limits of our HRGC-QMS/MS for PCDD/F correspond to between 0.3 and 3.0 pg/μl (except 6.0 pg/μl for octa-chlorinated dibenzofuran). We could detect no PCDD/F precursors from captan in the experiment performed at 400 °C. However, this was not the case for the experiment conducted at 600 °C. At this temperature, we detected a number of PCDD/F condensing in different parts of the experimental apparatus, as illustrated in Table 2. It is evident that MCDD/F dominate the distribution of the PCDD/F congeners in our experiment. This is consistent with higher production of benzene and CB than DCB, as evidenced in gaseous and VOC results. These results have also helped us to evaluate the effectiveness of the condensation and trapping of PCDD/F congeners in our system. The amount of captan participated in the experiment was 14.5 mg, which leads to a PCDD/F yield (w/w) of 19.8 ng per mg captan. From the measurements, we find that most of PCDD/F were trapped in the XAD-2 resin tube with no breakthrough into the solvent trap. Prior to the resin trap, the results indicate a small portion of PCDD/F condensing in both reactor tube and the PTFE tube.

Table 2. Quantification of detected PCDD/F (ng)

Congeners	Reactor tube	PTFE tube	XAD-2	Solvent trap	Subtotal
MCDF	5.94	34.4	186	1.54	n.d.
MCDD	0.35	2.01	7.73	0.08	n.d.
DCDF	10.9	21.2	7.72	n.d.	n.d.
DCDD	1.12	3.81	0.16	n.d.	n.d.
TriCDD	0.32	0.23	n.d.	n.d.	n.d.
TCDF	3.24	0.15	n.d.	n.d.	n.d.
Sum					288

n.d. - not detected or below limit of detection

MCDD/F, DCDD/F, TriCDD/F and TCDF denote mono, di, tri and tetra chlorinated dibenzo-*p*-dioxins and dibenzofurans

The formation of PCDD/F is expected to increase up to 700 °C. However, the construction of the apparatus, in particular the PFA fittings, prevents us from reaching 700 °C, to confirm this expectation.

The experimental measurements with the assistance of quantum chemical calculations prompt us to make the following comments about the decomposition processes of captan: HCA might be formed through the combination of two CCl_3 radicals. The CCl_3 radical can also react rapidly with O_2 to produce phosgene. These two products suggest the existence of the CCl_3 radical in the oxidative decomposition of captan, indicating the cleavage of the S-C bond. The calculated bond energy of S-C amounts to 55 ± 2 kcal/mol (0 K), the lowest bond energy in the captan structure. The presence of several sulfides suggests the concomitant oxidation of the active sulfur site resulted from the S-C bond fission. At higher temperature, HCA might gradually lose chlorine in a radical process, leading to the formation of TCE. Aromatic compounds indicate a facile abstraction of hydrogen atoms on the cyclohexene ring in the captan structure by radicals.

4. Conclusion

In this paper, we described a laboratory-scale apparatus, equipped with a sampling train to capture a wide range of products of the thermal decomposition of captan under oxidative conditions. We have assembled μGC , FTIR, IC, HRGC coupled to quadrupole MS (HRGC-QMS), as well as HRGC connected to an ion trap MS/MS (HRGC-MS/MS) analyses, and performed preliminary quantum chemical calculations to elucidate the experimental observations. Several toxic air pollutants, VOC and PCDD/F were identified and quantified in the experiments at two temperature levels. The quantitative results obtained from this study may contribute an improved understanding of captan combustion and provide useful information in evaluating its potential hazards to the public health and the surrounding environment.

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Appendix

The analysis of PCDD/F was performed on Varian CP3800 GC coupled by a transfer line (270 °C) to a Saturn 2000 (Varian) ion trap, MS/MS. The sample (1 μL) was introduced into an injector (280 °C) operated in a splitless mode. Chromatographic separation was achieved with a VF-5ms capillary column (60 m length, 0.25 mm i.d., 0.25 μm film thickness) with helium as the carrier gas (1 mL/min). The oven temperature program induced 80 °C (held for one min), then a rise to 235 °C (held for 10 min) at 10 °C/min, subsequent increase to 275 °C (held for 9 min) at 5 °C/min and then to 310 °C (held for 6 min) at 10 °C/min. We maintained the ion trap and manifold temperatures at 200 °C and 80 °C, respectively. We optimised the method and have quantified PCDD/F with standards obtained from Wellington Laboratories (Ontario, Canada). Table 3 lists daughter ions deployed for the quantification; i.e., parent minus COCl ($M-\text{COCl}$).

Table 3 Parent and daughter ions for mono-tetraCDD/F

Congener group	Base peak (<i>m/z</i>)	Parent ion (<i>m/z</i>)	Daughter ion (<i>m/z</i>)
MCDF	<i>M</i>	202	139
MCDD	<i>M</i>	218	155
DCDF	<i>M</i>	236	173
DCDD	<i>M</i>	252	189
TriCDF	<i>M</i>	270	207
TriCDD	<i>M</i>	286	223
TCDF	<i>M</i> +2	306	243
TCDD	<i>M</i> +2	322	259