

Thermal Degradation and Combustion Behavior of Antifungal Pesticides: Triadimenol and Tebuconazole

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Pesticides and plant protection products are widely used in modern industrial agriculture. Unfortunately, the thermal degradation and combustion of that chemicals can lead to emission of various toxic products that may cause a threat to humans and to the environment. Unwanted combustion can occurred during incidents, accidents or major accidents. Therefore, the determine flammability behaviour and knowing what thermal degradation products may be formed are significant for an analysis and risk management of production processes, storage and distribution of those chemicals.

In this paper, the thermal degradation and combustion of two of antifungal pesticides – triadimenol and tebuconazole, and plant protection products contain that substances were investigated. Measurements made by the cone calorimeter were used to determine the parameters associated with the rate of heat release from selected plant protection products. The determined parameters facilitated drawing conclusions on the size of the fire, its growth rate and consequently, the quantity and quality of the smoke emission. The Simultaneous Thermal Analysis that combines thermogravimetry and differential scanning calorimetry was used to determine thermal characteristics of pesticides and plant protection products. The products obtained from the thermal degradation were analyzed by infrared spectroscopy with Fourier transformation. Moreover the steady state tube furnace (ISO TS 19700) specifically to generate products from real fires under different conditions. The samples containing toxic products were analyzed by gas chromatograph with mass spectrometer .

The obtained results showed that pesticide undergo both thermal degradation and oxidation during thermal degradation in air. The type and yields of thermal degradation and combustion products depended most strongly on a temperature and oxygen concentration during experiment. The main substances identified under all tested conditions were: substituted benzenes, aldehydes, aliphatic hydrocarbons and polycyclic hydrocarbons

1. Introduction

The use of pesticides in agriculture is a common practice to protect crops all over the world. Triazoles are a class of fungicides largely used in agriculture as crop protection products. Their antifungal activity is due to their ability to inhibit the P450 enzyme (CYP51), which blocks the conversion of lanosterol to ergosterol causing disruption of fungal wall (Di Renzo et al., 2007). But the inhibition potency of these triazole fungicides is not limited to fungi, they may also inhibit other P450-mediated activities resulting in various adverse effects (Robinson et al., 2012). Triadimenol (TRI) and tebuconazole (TEB) are both triazole fungicides, which are applied on a number of crops such as grapes, wheat, rice, fruits, and vegetables because of their broad-spectrum antifungal activity (Yu et al., 2013). The structures of that pesticides are presented in Figure 1. Triadimenol is a mixture of two diastereomers, isomer A (erythro-configuration, SS- and RR-form) and isomer B threo-configuration, RS- and SR-form). Isomer A has a higher level of biological activity than isomer B. Each isomer is in itself a racemic mixture of two optical isomer forms. The ratio of the two isomers in the currently manufactured material is $\approx 80\%$ isomer A: $\approx 20\%$ isomer B (hereafter referred to as 80:20 material) (Burger and Boom, 2000). Triadimenol is also used in chemicals that kill or inhibit the growth of fungi on wood, plastics, or other materials, in swimming pools, etc. (Zhao et al., 2017).

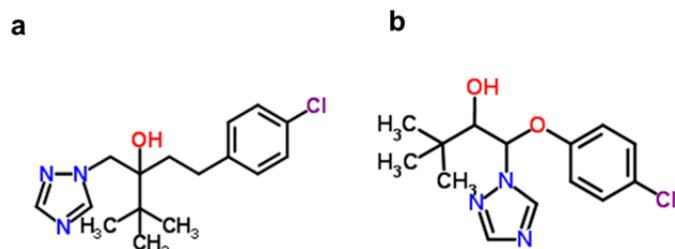


Figure 1: Structure of triadimenol (a) and tebuconazole (b)

In addition to the potential for causing incapacitation, injury and death, fires and fire effluents contain products emitted during thermal degradation and combustion of pesticides, may also cause harm to the environment. Several large fires have highlighted the often severe, widespread and prolonged contamination of the atmosphere, soil and water courses with the resulting ecological damage (Stec and Hull, 2010). The literature related to thermal degradation and combustion of pesticides (Chen et al. 2012; Sankowska et al., 2017, Summoogum et al., 2011) reports different burning behaviour and toxic product yields depend most strongly on a few factors. Material composition, temperature and oxygen concentration are normally the most important. The heteroatom, such as sulfur, nitrogen, phosphorous, fluorine, bromide or chlorine present in the structures of pesticides, can also convert into the large variety of toxic products (Stec and Hull, 2010).

To enable a realistic assessment of the toxicity and environmental impact of compounds, it is clearly important to understand the range and concentrations of chemical species likely to be produced in fires. Currently, the main species of interest for acute effects from exposure to fire effluents are: carbon dioxide (CO₂), carbon monoxide (CO), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen cyanide (HCN), hydrogen fluoride (HF), nitrogen oxide (NO), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), formaldehyde (HCHO) and acrolein (C₃H₄O). However this list is not exhaustive. Fire effluents also contain a number of carcinogenic and other chronic toxicants (persistent organic pollutants and polycyclic aromatic hydrocarbons (Fardell and Guillaume, 2010) .

In this work, the study of volatile and semi-volatile organic compounds emitted during thermal degradation and combustion of two of antifungal pesticides – triadimenol and tebuconazole and plant protection products contain that substances were done. The steady state tube furnace (ISO 19700:2007, Stec et al., 2008) has been used specifically to generate toxic products from real fires under different conditions. The released species have been sampling using solid phase microextraction technique (SPME) and identified using gas chromatography with mass selective detector (GC-MS). Moreover, in this work the thermal degradation process of these materials in air atmosphere was investigated using simultaneous thermal analysis (STA), which coupled thermogravimetric (TG) with differential scanning calorimetry (DSC) experiments. Measurements made by the cone calorimeter were used to determine the parameters associated with the rate of heat release from selected plant protection products. The determined parameters facilitated drawing conclusions on the size of the fire, its growth rate and consequently, the quantity and quality of the smoke emission.

2. Methodology

2.1 Materials

The tests were carried out for triadimenol (TRI) and tebuconazole (TEB) and for commonly used plant protection products contain that pesticides. Triadimenol (≥ 96 %) and tebuconazole (≥ 96 %) were purchased from Santa Cruz Biotechnology, Inc. (Germany). The plant protection products selected to studies were marked as PP1 and PP2. Both agents had the same composition according to the manufacturer. They contain tebuconazole (167 g L⁻¹), triadimenol (43 g L⁻¹), spiroxamine (250 g L⁻¹), N,N-dimethyl decanamide (> 20 %), alkylaryl polyglycol ether (>1 i < 25 %) and gamma-butyrolactone (>1 i < 15 %). Both were purchased from Bayer Crop Science (Germany).

2.2 Flammability test

Measurements made by the cone calorimeter were used to determine the parameters associated with the rate of heat release from samples. Tests were performed according to standard (ISO 5660-1:2002). During measurement, samples were placed on aluminum foil and treated with an external heat flux with a density of 35 kW m⁻² simulating thermal exposure during the first phase of a fire. Based on the results, the following parameters were estimated: Heat Release Rate – HRR (kW m⁻²), peak of Heat Release Rate – pHRR (kW m⁻²) time to peak of Heat Release Rate – t pHRR (s), Maximum Average Rate of Heat Emission – MARHE, Total

Heat Release –THR(MJ m⁻²), Ignition Time – It (s), Flame Out Time – F_{out} (s), Total Smoke Release – TSR (m²) and Fire Growth Rate – FIGRA (kW m⁻²s⁻¹).

2.3 Identification of thermal degradation and combustion products

In order to identify hazardous substances generated during thermal degradation and combustion of selected materials, measurements were performed using the simultaneous thermal analysis (STA, 449F3 Jupiter, Netzsch, Germany). The 10 mg samples were placed in aluminum oxide crucibles and heated at the rate of 10 °C min⁻¹ from room temperature (25 °C) to 900 °C. The flow rate of the air was 30 ml min⁻¹ and the nitrogen was 20 ml min⁻¹. To ensure the good reproducibility of the process, the experiments were performed at least three times. The volatile products evolved during thermal decomposition were analyzed by Fourier-transform infrared (FT-IR) spectrometer (Tensor 27, Bruker, Germany) coupled on-line to the STA instrument. The gas cell of FT-IR and transfer line were maintained at 200 °C. The spectra were recorded in the spectral range of 650 – 4000 cm⁻¹ with 16 scans per spectrum at a resolution of 4 cm⁻¹.

The thermal decomposition and combustion of selected materials was investigated by the steady state tube-furnace method. That method can be used to model a wide range of fire conditions by using different combinations of temperature, non-flaming and flaming degradation conditions and fuel/oxygen ratios in the tube furnace. These include the different types of fires, as detailed in ISO 19700:2007 (ISO 19700:2007, Stec et al., 2008). Samples of the material were combusted under steady-state conditions in one of three environments whose temperature and air flow are representative types of fire: oxidative pyrolysis, small flaming vitiated fire and post-flashover vitiated fire. The samples of fire effluents were taken from the mixing chamber of tube furnace by introducing the solid phase microextraction (SPME) device with the fiber to sampling port after 1 min from placing the sample of pesticide in the furnace heating zone. After introducing the SPME syringe to the mixing chamber, the products of thermal degradation were extracted on the SPME fiber coating. After sorption, the fiber was withdrawn from the chamber and desorbed immediately in the gas chromatograph injector for analysis. The chromatographic separation was achieved with an HP-5 MS fused silica capillary column (30 m × 250 μm × 0,25 μm film thickness) from Agilent Technologies (USA). The oven temperature was initially maintained at 40°C for 10 min, and then increased to 250 °C at a heating rate of 10 °C min⁻¹. Helium at a constant flow rate of 1 ml min⁻¹ was used as the carrier gas and the split ratio was 10:1. The separated compounds were then analyzed by the mass spectrometer, which was operated in electron ionization (EI) mode at the ionization energy of 70 eV. The mass spectra were obtained from m/z 15 to 350. Chromatographic peaks were identified through comparing the mass ions of each peak with NIST MS Library. On the basis of the NIST library, the highest possibility of product identification was chosen. Because the chromatographic peak area of a specific compound is correlated linearly with its quantity, and its concentration can be reflected by the peak area ratio. The summed identified peak areas were normalized to 100 % and the relative abundance of specific compound can be reflected by its peak area ratio.

3. Results and Discussion

3.1 Fire behaviour

The results of the cone calorimeter measurements was the set of parameters characterizing the behaviour of plant protection products under the influence of intense radiant heat, Table 1.

Table 1: Fire behaviour parameters of plant protection products

	I _t (s)	F _{out} (s)	MARHE (kW m ⁻²)	HRR (kW m ⁻²)	pHRR (kW m ⁻²)	t-pHRR (s)	FIGRA (kW m ⁻² s ⁻¹)	THR (MJ m ⁻²)	TSR (m ² m ⁻²)
PP1	12	163	574	447	1019	68	14,9	66,3	769
PP2	11	164	538	433	943	65	14,5	34,7	750

The obtained results showed that both products have very similar characteristics of the combustion process. The equal content of active ingredients, i.e. tebuconazole, spiroxamine and triadimenol in these plant protection agents, means that both the ignition time and the development of the combustion process of these mixtures is very similar. The very low flash point and the very high heat release rate of the these plant protection agents are primarily responsible for the presence of organic solvents and spiroxamine. However, it is worth paying attention to similar amounts of smoke generation. On the basis of the obtained results and chemical structure of active ingredients of the tested plant protection agents, it can be concluded that the high amount of fumes generated during the combustion of tebuconazole and triadimenol is related to the presence of aromatic rings and halogen substituents.

3.2 Thermal analysis

The results of thermal degradation of the selected materials performed under air atmosphere are shown in Figure 2. The course of differential thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC) curves suggest that the thermal degradation of triadimenol and tebuconazole is two-step process. Whereas the degradation of the tested plant protection products is the more complex process. The obtained results suggest that the samples exposed to heat in air undergo both thermal degradation and oxidation. Moreover, the weight loss is related to the emission of gaseous molecules, because there is no solid residues.

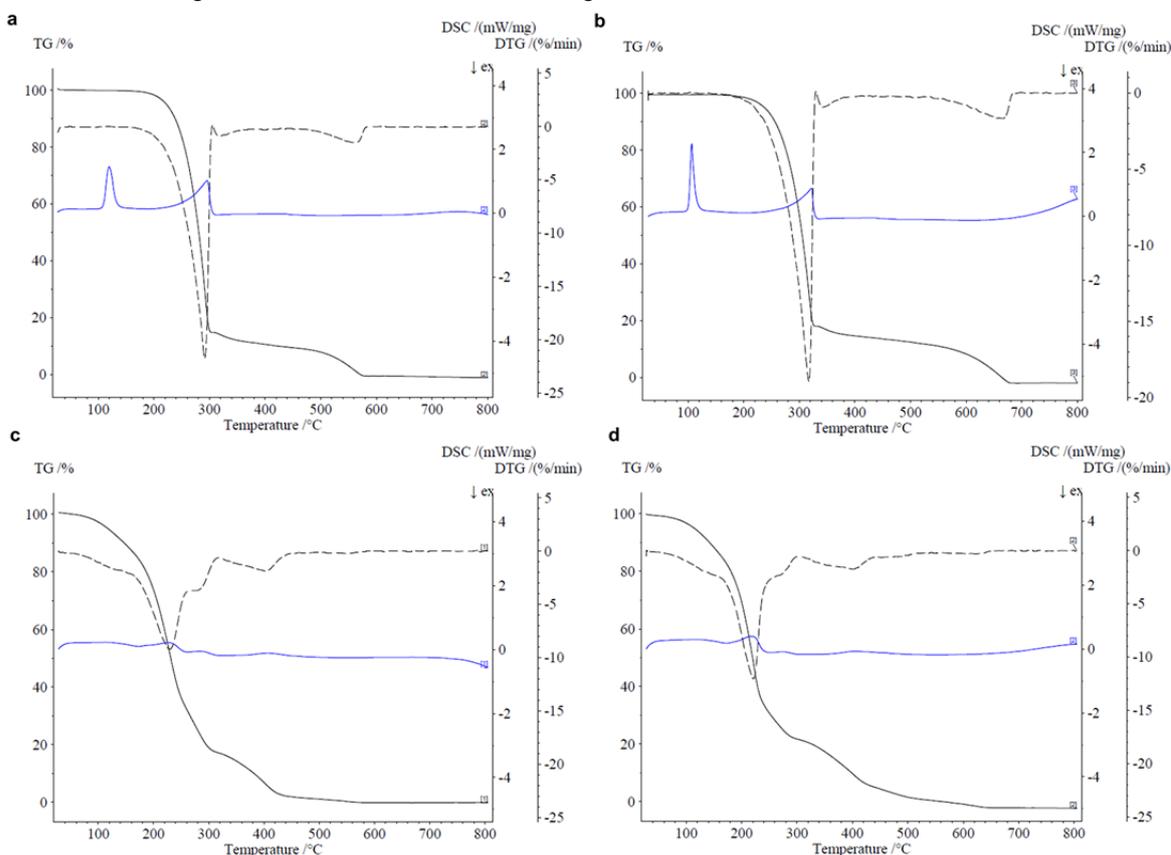


Figure 2: TG, DTG and DSC curves of triadimenol (a), tebuconazole (b), PP1 (c) and PP2 (d)

3.3 Analysis of fire effluent

Based on the obtained results, it was found that the quantity and type of products detected in the fire effluents emitted during thermal degradation and combustion of selected materials strongly depended on experiment conditions, Figure 3.

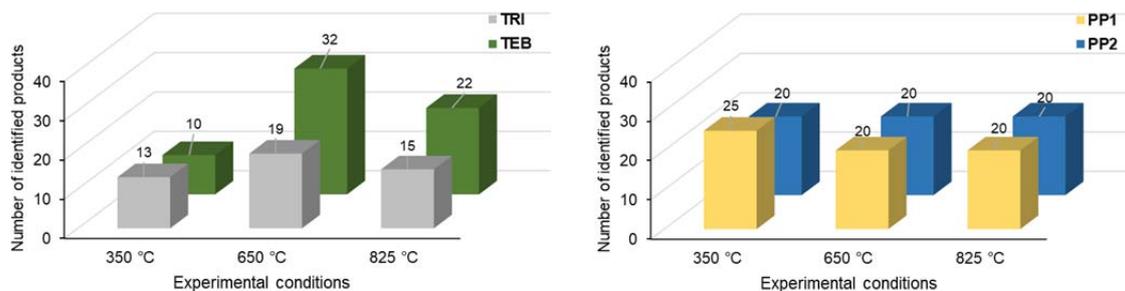


Figure 3: The number of thermal degradation products identified in fire effluents

The largest member of species were detected in the samples emitted in conditions representative small flaming vitiated fire (temperature = 650 °C, primary air flow = 2 L min⁻¹). While the number of products released during the plant protection products degradation practically did not depend on the conditions of the measurements. The examples of gas chromatography data of the gas samples released during thermal decomposition of selected materials are shown in Figure 4. Only during thermal decomposition of PP1 under oxidative pyrolysis (temperature = 350 °C, primary air flow = 2 L min⁻¹), in fire effluents more chemicals were identified.

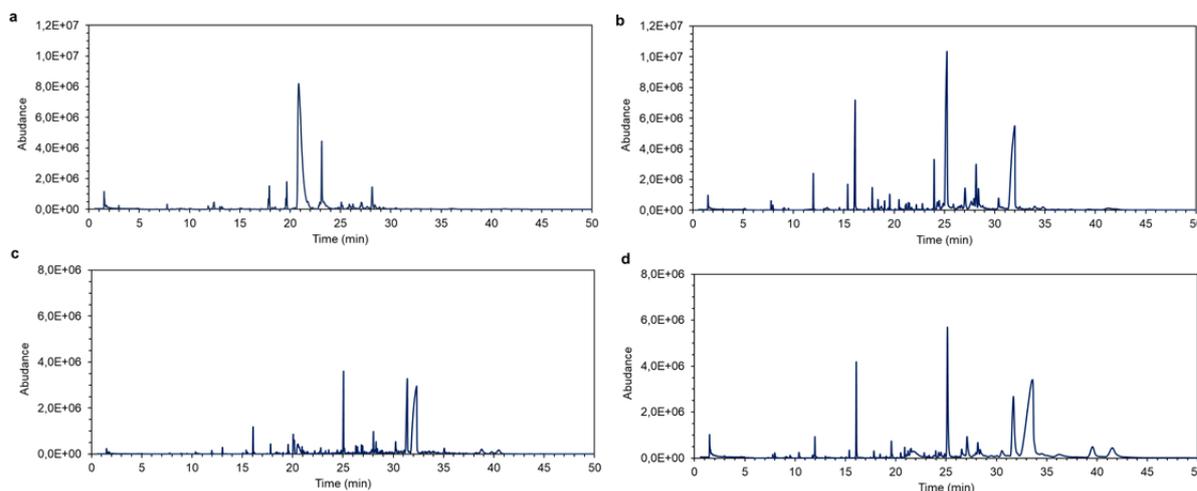


Figure 4: Total ion chromatograms from GC-MS analysis of fire effluents obtained during thermal degradation of triadimenol (a), tebuconazole (b), PP1 (c) and PP2 (d). Thermal degradation took place in conditions representative small flaming vitiated fire

The main thermal degradation product of triadimenol was 4-chlorophenol, which was presented in all testes conditions. Another main identified substance present in fumes emitted during the degradation of triadimenol during oxidative pyrolysis were: 4-chlorobenzaldehyde, 1-ethyl-1H-pirol-2,5-dione, 1-chloro-4-etoxybenzene and 2,2'-dimethylpropanoic acid 4-chlorophenyl ester. The 4-chlorobenzaldehyde was also detected in products released in conditions representative small flaming vitiated fire and post-flashover vitiated fire (temperature = 825 °C, primary air flow = 2 L min⁻¹). When the decomposition took place under conditions representative small flaming vitiated fire also large amounts of 4-chlorobenzofuran and 5-chloro-2-methylbenzofuran have been formed. In the gases emitted at 825 °C the chemicals such as: 4-chlorobenzofuran, 5-chloro-2-methylbenzofuran and many substances from the group of polycyclic aromatic hydrocarbons (naphthalene, acenaphylene, fluorene and anthracene) were identified.

The main products of thermal degradation of tebukonazol occurring in conditions representative oxidative pyrolysis were: 1-chloro-4-ethenylbenzene, 4-chlorobenzaldehyde, 2-chloro-hydroxyaminonitrile and 1-(4-chlorophenyl)ethanone. All these chemicals were presented in large amounts in gases released when the decomposition took place under small flaming vitiated fire conditions. But in that situation the main thermal degradation product was 1-chloronaphthalene. When the decomposition took place under post-flashover vitiated fire conditions large amounts of 1-chloronaphthalene, 4-chloro-1,1'-biphenyl, 2-chlorodiphenylmethane and 1-chloro-4-ethenylbenzene have been formed. In the gases also polycyclic aromatic hydrocarbons were detected.

Among the identified products formed during the decomposition of PP1 and PP2 in the largest amount were detected 4-(1,1-dimethylethyl)-cyclohexanone. This compound probably was formed as a result of the degradation of the spiroxamine. The 4-(1,1-dimethylethyl)-cyclohexanone is a harmful substance that is toxic to aquatic life, causing long-lasting effects. In the decomposition products, p-tetr-butylphenol was also detected, which was also formed as a result of the decomposition of spiroxamine. P-tert-butylphenol, like other phenolic compounds, is a harmful substance, and has the toxic effect on aquatic life, causing long-lasting effects. In addition, 4-chlorobenzaldehyde and 1-chloro-4-ethenylbenzene were formed in considerable quantities during the decomposition of plant protection products, which substances were also identified in the decomposition products of the active substances from the group of fungicides: tebuconazole and triadimenol. N, N-dimethyldecanamide and gamma-butyrolactone were also identified in the mixture of emitted gases and fumes, these substances were part of the tested plant protection products. Moreover, during the thermal

decomposition of PP1 and PP2, a wide range of compounds from the group of polycyclic aromatic hydrocarbons was formed.

4. Conclusions

The obtained results showed that triadimenol and tebuconazole and plant protection products contain that substances undergo both thermal degradation and oxidation during thermal degradation in air. The type and yields of thermal degradation and combustion products depended most strongly on the conditions during experiment. The biggest number of products were detected in fire effluents when the degradation occurred under conditions representative small flaming vitiated fire. In gaseous mixture: phenolic compounds (phenol, p-cersol, 2,6-dichlorophenol, 4-chlorophenol and 4-chloro-2-methylphenol), oxidation product of phenol – p-benzoquinone, substituted benzenes and benzofurans were identified. Moreover many substances from the group of polycyclic aromatic hydrocarbons were presented in fire effluents (naphthalene, acenaphylene, fluorene and anthracene). In addition, significant amounts of chlorinated naphthalenes, biphenyl and dibenzofuran were also detected. It should be noted that in fire effluents may also be presented polychlorinated derivatives of dibenzofuran (PCDF), which are compounds with a structure and properties similar to dioxins.

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