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Thermal degradation of Fenitrothion: Identification and eco-toxicity of decomposition products

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ABSTRACT

The thermal decomposition of Fenitrothion [phosphorothioic acid O,O-diethyl O-(3-methyl-4-nitrophenyl) ester] was investigated. Results obtained by different scale calorimetric techniques show that the thermal decomposition of Fenitrothion involves two main steps. Intermediate and final thermal degradation products formed during isothermal and adiabatic thermal decomposition experiments were identified. The eco-toxicological profile of the decomposition products was assessed experimentally and compared to results obtained with a predictive software (ECOSAR). A specific index was defined to assess the change in ecotoxicity profile of decomposition products with respect to the original compound.

1. Introduction

The hazard related to the storage and handling of pesticides is well known [1,2]. Toxicity, thermal instability and reactivity caused several accidents during the production, the transport and the storage of these compounds [3]. Particularly severe accidents were caused by the atmospheric dispersion of decomposition products formed as a consequence of fire or of runaway during storage or mixing processes [4,5]. The Seveso accident [6], that gave the name to the European Directive on the control of major accident hazards involving dangerous substances [7], is a well known example of the very severe hazards that may derive from these accidental scenarios. Several studies proposed methods for the identification of possible unwanted products formed in "out of control" conditions, mainly starting from past accident analysis, from the definition of experimental protocols and from simple predictive methodologies [4,8–12]. However, in spite of the relevant work carried out to develop and standardize experimental protocols and predictive methods, scarce data are often available on the decomposition products that may be formed due to the thermal degradation or partial combustion of chemicals.

In the present study, the thermal degradation and the decomposition products of Fenitrothion were investigated. Fenitrothion is an organophosphorus compound used to produce pesticides that find a number of applications in agriculture. Production of Fenitrothion is estimated around 15,000–20,000 tonnes/year [13]. Phosphorganic pesticides are well known for their hazard and several accidents related to the formation and dispersion of toxic decomposition products were recorded [14]. Different calorimetric techniques were applied to gather experimental data on the thermal decomposition behaviour of Fenitrothion. The decomposition products were identified by analytical techniques. The possible decomposition pathways of Fenitrothion were examined also on the basis of previous results obtained for dimethoate [15] and ethyl parathion [16]. The eco-toxicity of decomposition products was assessed using both theoretical calculations and experimental bioassays. The results allowed a screening of the hazard related to the possible formation and release of decomposition products in the loss of control of chemical industrial processes involving Fenitrothion. Specific attention was devoted to the comparison of the overall eco-toxicity of the mixture of decomposition products formed, in order to assess the presence and the importance of antagonistic or synergistic effects.

2. Experimental

2.1. Materials

Fenitrothion (CAS 122-14-5, 97% (w/w) technical purity grade) was purchased by Sigma–Aldrich. Standard samples of the

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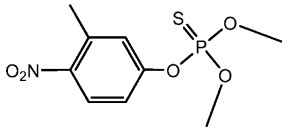
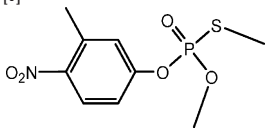
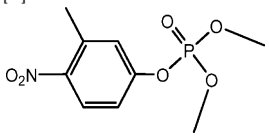
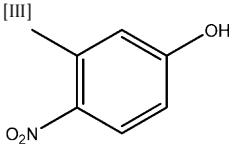
Table 1
Compounds identified during the first exothermal event in the isoperibolic (Radex) experiments performed on Fenitrothion.

Compound	Name/chemical formula (CF)/molecular weight (MW)/smile
 [I]	Fenitrothion O,O-dimethyl O-3-methyl-4-nitrophenyl phosphorothioate (CF: $C_9H_{12}NO_5PS$; MW = 277.23) S=P(OC)(OC)OC1=CC(C)=C([N+]([O−])=O)C=C1
 [II]	O,S-Dimethyl O-3-methyl-4-nitrophenyl phosphorothioate (CF: $C_9H_{12}NO_5PS$; MW = 277.23) O=P(SC)(OC)OC1=CC(C)=C([N+]([O−])=O)C=C1
 [III]	Dimethyl 3-methyl-4-nitrophenyl phosphate (CF: $C_9H_{12}NO_6P$; MW = 261.17) O=P(OC)(OC)OC1=CC(C)=C([N+]([O−])=O)C=C1
 [IV]	3-Methyl-4-nitrophenol (CF: $C_7H_7NO_3$; MW = 153.14) OC1=CC(C)=C([N+]([O−])=O)C=C1