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Toxicological Characterization of the Thermal Decomposition Products of Chemicals: a New Approach to an old Problem

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Different calorimetric techniques coupled with chemical analyses and ecotoxicological bioassay led to the proposal of suitable protocol for the definition of a KPI (Key Process Index) useful to rank a compound in respect to the toxicological profile of its thermal decomposition products. Fenitrothion was used as example and showed to decompose through a series of two main processes, the first being less severe than the second. It is demonstrated that similar ecotoxicological results can be gathered both using adiabatic and Isothermal conditions. This allows to exclude *a priori* the necessity of carrying out the more difficult and time and money consuming adiabatic experiments. The analytical characterization of the samples collected during a series of isoperibolic (*quasi*-isothermal) experiments allowed to calculate, using the software ECOSAR, the toxicological profile of the intermediate compounds.

1. Introduction

In the present work the results of an investigation on the thermal decomposition of Fenitrothion are reported. Incidental events in which unpredictable dangerous substances are released to the environment imposes the characterization of the thermal decomposition product distribution (Directive 96/82/EC, 1997, European Comm. Env., 2003). A literature survey indicated that some attempts have been done in the past to develop suitable procedures for the identification and prediction of hazardous substances which form during the loss of control of a chemical process (Cordella M. et al., 2009, Andreozzi R. et al., 2006). Nevertheless, to date neither suitable experimental protocols nor theoretical tools devoted to assess or foresee the possible compounds that could be formed in such events have been still developed. This is principally due to the difficulties in the analytical resolution of the complex mixtures resulting from the thermal decomposition processes and the definition of the experimental conditions that could lead to samples representative of the worst scenario. Due to these difficulties for the most part of the chemicals the section of their Material Safety Data Sheet dedicated to the "decomposition products" contain no information or only scant data mainly for the evolved gases. The present paper aims at showing the importance to fill this gap of knowledge and propose a new

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approach to face the problem This is done by using some algal bioassays in the case of the thermal decomposition of Fenitrothion (Bretherick L., 1990).

2. Experimental

2.1 Calorimetric and analytical techniques

All experiments were carried out using samples of fenitrothion (97% w/w technical purity grade). Depending by the particular use of the samples they were prepared using as solvent (analytical grade) either Dimethyl sulfoxide (DMSO) or methanol. When available the standards were purchased from Sigma Aldrich (Fenitrothion, dimethyl 3-methyl-4-nitrophenylphosphonate and 3-methyl-4-nitrophenol while in the other cases they were prepared by means of a suitable Thin Layer Cromatography (TLC) procedure. A series of calorimetric runs were performed using different techniques. Adiabatic runs were carried out by means of an Accelerating Rate Calorimeter (ARC) by Columbia Scientific Industries equipped with Hastelloy C bombs. A series of runs were also performed to the aim at assessing the toxicological profile of the intermediate decomposition products. In this case the samples were brought to the initial temperature ($T_{O,Ad}$), the instrument forced to the adiabatic mode and, after a period of time in these conditions, the reactor was quenched at ambient temperature. The samples were then collected in DMSO for the successive toxicological bioassays. Isoperibolic experiments were performed by means of a Radex Oven (Priestley I. et al., 2006) equipped with a Stainless Steel reactor. This system can be operated also in scanning mode. In the isoperibolic runs, were used samples of about 2 g. At the end of the isothermal time the reactor was quenched at room temperature and samples collected using 50 ml of methanol for the successive chemical analyses. Samples of about 0.1 g for the ecotoxicological tests were prepared in a similar way but using an oil bath at 140 °C heated by means of an Heidolf MR 3001 K heating plate. Fenitrothion was charged in sealed glass tube successively immersed in a bat oil for the desired reaction time. After a quenching the reaction mixture was collected using 5 ml of DMSO. DSC runs were carried out using a Perkin Elmer 8000 (Samples of 3÷6 mg were charged in a sealed Stainless Steel High Pressure capsule) Dynamic runs were performed starting from 50 °C with an Heating Rate β=5 and 10 °C min^{-1} up to 320 °C. Isothermal runs were performed at temperatures of 135, 140, 145 and 150 °C over different period of time (190-700 min).

2.2 Ecotoxicological Bioassay

Preliminary dose-response experiments of fenitrothion toxicity towards *Pseudokirchneriella subcapitata* were carried out using either EPA medium (EPA, 2001) or BBM (Nichols H.W., 1973). The results obtained indicate that salt concentration in the medium does not influence the toxicity of the selected compounds and in 96-h end-point experiments algae grew at a faster growth rate with BBM. For this reason all the following experiments were performed with this latter medium. Based on the preliminary results of dose-response experiments, for the algal bioassays, each solution of the selected compounds was prepared by dissolving a known quantity of compound in BBM to have a final concentration of 32 mg l^{-1}. The toxicity test was based on the measurement of the growth inhibition of the green unicellular alga *P. subcapitata*, strain UTEX 1648 (EPA, 1996). Algal inocula corresponding to 10,000 cells/ml from laboratory cultures in mid exponential phase were grown in 100 ml Erlenmeyer flasks containing 50 ml of Bold Basal Medium (BBM) and the testing compound at the following concentrations: 32, 16, 8, 4 and 2 mg l^{-1}. The compounds tested were FNT after adiabatic treatment at T=136, 143, and 201°C or FNT after isothermal treatment at 140 °C at time 0, 75, 120, 150, 195 and 240 min. The flasks were incubated on a shaking (~ 100 RPM) apparatus at 24 °C under continuous illumination at a light intensity of 90 μEs^{-1} m^{-2}. The tests were carried out in triplicate and in axenic conditions. A series of controls containing only BBM and the algal inocula, were also prepared. The algal growth was followed after 96 h from the addition of the compounds by measuring the *in-vivo* chlorophyll fluorescence using a fluorometer (Turner, model Aquaflor, Turner Designs CA, USA). Data from growth inhibition tests were analyzed using Toxstat 3.4 (Western Ecosystems Technology, Inc., Cheyenne., WY): after verifying normality (X^2 test) and homogeneity of variance (Bartlett's test). The EC_{50} was determined using the ICPIN program (Norberg-King T. J., 1993) which calculates the EC values by linear interpolation and 95% confidence intervals by the bootstrap method.

3. Discussion and Results

As it was clearly pointed out in a preliminary Radex run performed in scanning mode (Starting Temperature: T_{Start}=25 °C, heating rate: β=3.3 °C min^{-1}) on a sample of pesticide (m_{sample}=1.0399 g), that the decomposition of Fenitrothion develops violently through two exothermic phases. This behaviour was confirmed both in two dynamic DSC runs (samples of about 4 mg, heating rates: 5 and 10 °C/min) and in adiabatic conditions (sample mass: m_s=1.36 g, thermal inertia Φ=2.8) (Fig. 1). DSC results allowed to calculate the following heats of reaction for the first and second peaks identified: $\Delta H_{R,1}$=314±6 J/g, and $\Delta H_{R,1}$=1359±34 J/g

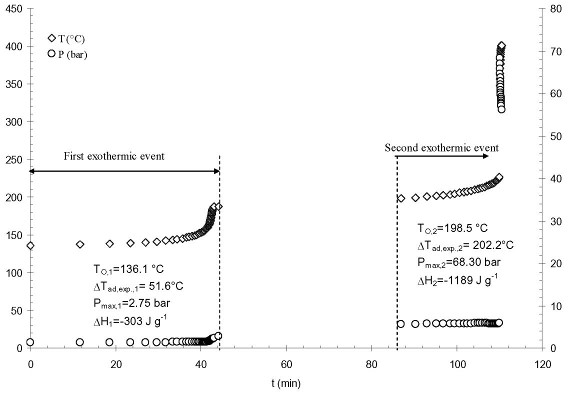

Figure 1: Temperature and pressure plots versus time obtained in an ARC run carried out on a sample of Fenitrothion

Mixtures collected after quenching at the end of the first adiabatic exothermic event were submitted to GC/MS analysis and allowed to determine the following decomposition products: [1] substrate, [II] O,S dimethyl O-3-methyl-4-nitrophenyl phosphorothionate, [III] dimethyl 3-methyl-4-nitrophenyl phosphate, [IV] 3-methyl-4-nitrophenol. The separation of the mixture indicated the presence of a compound for which it has not been possible to write a reliable structure. High e/m fragments in

GC/MS spectrum and acid catalyzed hydrolysis that gives rise to the formation of 4 methyl-nitrophenol with a ratio P/*4 methyl-nitrophenol*>1 seems to suggest a polymeric structure ([V] *polymer*). On the base of the results collected during the DSC and Radex dynamic runs a series of isothermal experiments were carried out at different temperatures (135, 140, 145 and 150 °C) using samples of abut 5.0 mg. In these runs the specific heat power signal q=q(t) was acquired at Temperature $T=T_{Isotherm}$. Conversion degree was calculated by means of the equation: $\alpha = \frac{\int_0^t q(t)\,dt}{-\Delta H_R}$ where $-\Delta H_R$ is the heat of reaction that in this case resulted: $-\Delta H_R = (324 \pm 5)$ J g^{-1}. Two Radex isoperibolic runs were performed on samples of 2.0 g of Fenitrothion at 140 and 150 °C. In both case (symbols in Fig. 2) the conversion of the substrate was determined by means of chemical analysis. As it is evident considering these results, the conversion evaluated at 140 and 150 °C are compatible with tat gathered in the Isoperibolic RADEX run performed at the same temperatures.

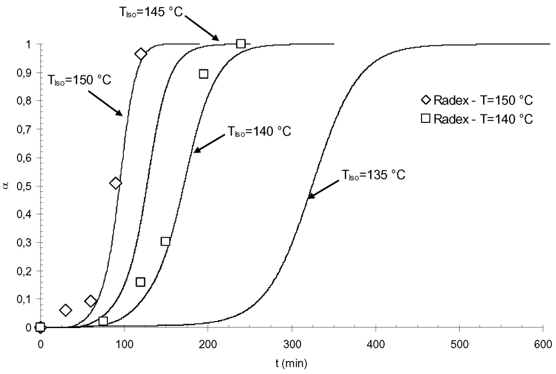

Figure 2: Conversion of Fenitrothion versus time in isothermal DSC runs (Continuous line) and isoperibolic conditions (Symbols) at different temperature.

It has been also assessed that the decomposition products are the same as determined at the end of the first adiabatic event.

3.1 ECOSAR Calculations

ECOSAR is a freely software by US EPA (EPA, 2009). It allows the evaluation of different ecotoxicological indexes concerned with a target molecule considering as input its structure given in "smile" notation. The program is based upon structure–activity relationships (SARs). This package was used to evaluate the EC_{50} (Green Algae-96 h) for the substances identified. For the compound V have been considered four different structures. Depending on the particular structure assumed, the EC50 can result either greater or lower than the substrate. This circumstance suggest that when the decomposition products distribution is not completely and rigorously known the results that came from theoretical evaluations can lead to erroneous conclusions.

3.2 Ecotoxicological bioassay

Since the isothermal DSC results and Radex isoperipolic runs give the same results in term of conversion of the substrate, to the aim at simplifying the procedure, the isothermal samples (about 0.1 g) submitted to toxicological evaluations were prepared using a simple bath oil at 140 °C and using the following reaction time: 0, 75, 120, 150, 195 and 240 min (Samples 0, 1, 2, 3 4, and 5). The results of these Ecotoxicological tests are shown in Fig. 3 where are reported the values of $\lambda^{(i)}_{Isothermal}=EC_{50}^{(i)}/\ EC_{50}^{(0)}$; i=0 … 5. Adiabatic experiments devoted to ascertain the toxicological profile of the samples collected during the first decomposition step of fenitrothion were carried out using the same conditions adopted for the run reported in Fig. 1. Three experiments were performed interrupting the runs at 136.1, 142.9 and 201.5 °C (Samples 0, 1 and 2). Samples were collected using DMSO and then submitted to toxicological bioassay. The results of these ecotoxicological analysis are reported in Fig. 4. Also in this case it has been defined the following parameter: $\lambda^{(j)}_{Adiabatic}=EC_{50}^{(j)}/\ EC_{50}^{(0)}$; j=0 …2

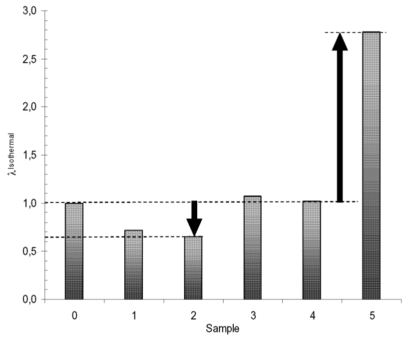

Figure 3: Toxicological Indexes in Isothermal conditions

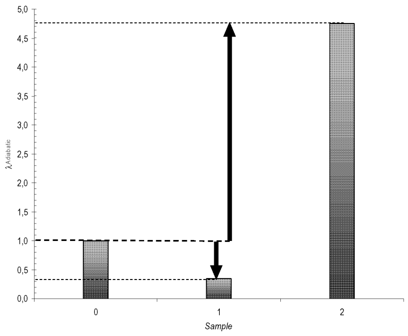

Figure 4: Toxicological Indexes in adiabatic conditions

The results reported above allow us to define and calculate the following indexes: $L_{Isothermal}=\min(\lambda_{Isothermal})=0.70<1$ (1) and $L_{Adiabatic}=\min(\lambda_{Adiabatic})=0.35<1$ (2). Both these indicators point out that the thermal decomposition of fenitrothion lead to generation of reacting mixtures more dangerous than the initial substrate. $L_{Isothermal}$ is of the same order of magnitude of $L_{Adiabatic}$ thus the first could be assumed as a valid key process indicator since it represent an objective parameter to characterize the thermal decomposition products of a substance.

4. Conclusions

The results of the present investigation indicate that in adiabatic conditions at temperature higher than 136 °C Fenitrothion undergoes a thermal decomposition process. This process is characterized by two exothermic events during which relevant amounts of gases are evolved. A suitable protocol devoted to characterize from a toxicological point of view the product distribution that generate in its thermal decomposition has been developed. The attention has been focused on the first exothermic event. The protocol developed consist in the following steps:

[a] run one (or more) dynamic DSC run

[b] at a temperature T_{Iso} around the on set temperature determined in [a], run a DSC isothermal run. Calculate the conversion vs time curve

[c] adopt the conversion vs time curve determined in [b] to run a series of isothermal runs at T_{Iso} (using simple apparatus such us an Oil Bath). Four or five samples at different conversions (say 0, 25, 50, 75, 100%) are enough to cover all the possible product distribution scenarios.

[d] submit the samples collected in [c] to the desired toxicological bioassay (in our case was assessed the EC50 (96 h))

[e] derive a Key process indicator ($L_{Isotherm}$) as defined in (1)

$L_{Isothermal}$ could be used as a reliable KIP since it has been demonstrated (using as example the case of fenitrothion) that the adiabatic conditions (worst scenario) are not more conservative from a toxicological point of view in respect to the isothermal conditions.

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