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The thermal decomposition of dimethoate

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Abstract

The thermal decomposition of dimethoate, an organophosphorus pesticide, has been studied with the aim at assessing the reaction kinetics, the energy released during the process and the decomposition products. Dimethoate shows a marked tendency to undergo thermal decomposition at temperature higher than 369 K. A moderate pressure increase has been recorded at the end of all runs. Many thiophosphoric compounds have been identified among the decomposition products.

Keywords: Dimethoate; Organophosphorus pesticides; Thermal decomposition; Kinetics; Calorimetry

1. Introduction

Large amounts of hazardous substances such as pesticides are handled and stored every day in chemical plants and warehouse as a consequence of their massive use in the agricultural field. It has been reported in the past that fire occurred in a certain number of these installations involving large quantities of chemicals (Christiansen [1]). With respect to these events some studies appeared in the literature about hazardous combustion products of selected pesticides (Kakko et al. [2], Smith-Hansen and Jorgensen [3]).

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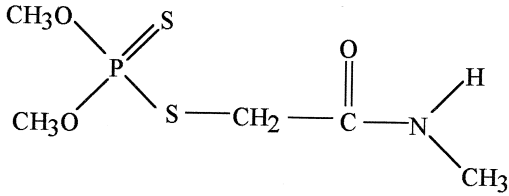


Fig. 1. Molecular structure of dimethoate (MW: 229.11 g mol^{-1}).

Unfortunately, the above studies supply only a limited part of the information required for a safe handling and storage of such substances. In fact, at present, a huge gap of knowledge is recorded on the behaviour of the most part of the pesticides, when they are involved in a fire.

A similar lack of information is also recorded referring to the pesticide capacity to undergo thermal explosion at temperature values higher than the ambient and which could be reached as a result of a fire in the neighbour of the storage vessels.

In the present paper, the results of an investigation about the thermal behaviour of *O*,*O*-dimethyl-*S*-(*N*-methylcarbamoylmethyl)phosphorodithioate (dimethoate, DIM), an organophosphorus insecticide (Fig. 1), are reported.

The work aims at assessing the reaction kinetics of the thermal decomposition, the energy released during the process and the distribution of decomposition products which represent a solid basis of knowledge for planning a more safe handling and storage of dimethoate.

The thermal stability of a dimethoate and β-cyclodextrin mixture has been also investigated, because it has been reported that the presence of β-cyclodextrin increases the thermal stability of the dimethoate (Maeda et al. [4]).

2. Experimental

All the experimental runs have been performed by means of an A.R.C. calorimeter (by Columbia Scientific Industries) and/or a PC Combilab (by Systag) equipped with a Radex oven.

The Radex runs have been performed both in *quasi*-isothermal and in scan mode. For each *quasi*-isothermal run, 1.2 g of dimethoate have been kept at the reaction temperature for a fixed time.

The solid residues coming from *quasi*-isothermal runs have been dissolved in methanol and submitted to GC-MS analysis. This has been carried out with a Saturn 2000 apparatus (by Varian) using a DB5 column with an Ion Trap detector. The flow rate of carrier gas (Helium) was 10 ml min^{-1}. For each analysis, the following temperature ramp has been used: 313 K for 40 min, 5 K min^{-1} up to 473 K, 473 K for 32 min, 5 K min^{-1} up to 523 K, 523 K for 10 min.

All the A.R.C. runs have been performed in Hastelloy C bombs with the following set parameters: wait time 10 min, heat step temperature 10 K, heat rate threshold value 0.02 K min^{-1}.

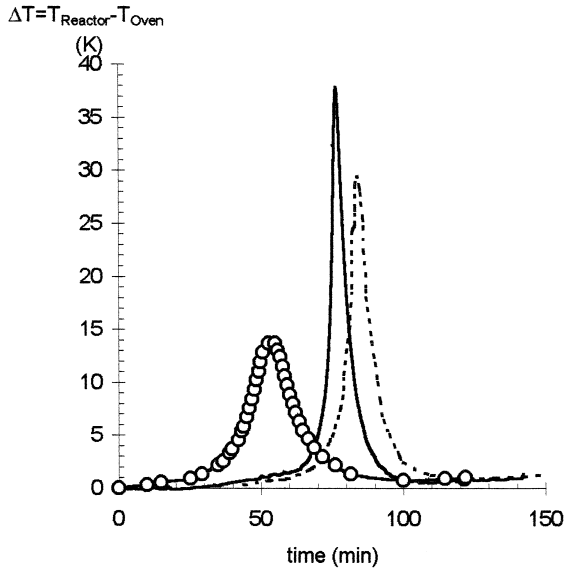


Fig. 2. (————) Scan on dimethoate; scan on samples coming from *quasi*-isothermal runs at: (—) 383 K for 60 min, (–○–) 388 K for 75 min.

The conversion of dimethoate in *quasi*-isothermal runs has been assessed by evaluating its unreacted fraction. To this purpose the samples coming from *quasi*-isothermal runs have been submitted to a temperature scan from 298 K to 523 K at a heating rate of 200 K h^{-1} and resulting peaks (Fig. 2) were integrated to evaluate the area. The conversion has been evaluated by the following Eq. (1):

$$u = 1 - \frac{A_T}{A_O} \tag{1}$$

where A_0 is the reference area which is derived by integrating the peak obtained in the scanning run with 1.2 g of dimethoate (Fig. 2), not submitted to *quasi*-isothermal heating. The dimethoate pesticide (97% by weight) was supplied by Caffaro.

3. Results and discussion

The experimental results of an A.R.C. run performed on a dimethoate sample (1.52 g) ($C_{ps} = 2.1$ J g^{-1} K^{-1}) in a Hastelloy C bomb ($C_{pb} = 0.50$ J g^{-1} K^{-1}) with a thermal inertia $\Phi = 2.6$ are reported in Fig. 3.

The on-set temperature was found at 369.5 K while the experimental adiabatic temperature rise was assessed to be $\Delta T_{ad,exp} = 97.6$ K from which a heat of reaction of $\Delta H_R = -122.1$ kJ mol^{-1} was calculated. A moderate pressure increase was recorded during the runs.

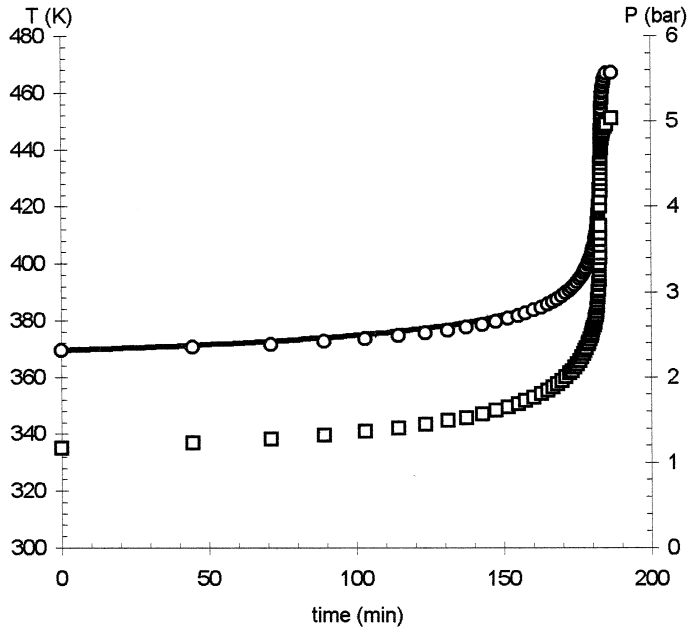


Fig. 3. Temperature and pressure plots versus time during an adiabatic A.R.C. run on dimethoate. (○) Temperature, (□) Pressure, (—) Calculated temperature.

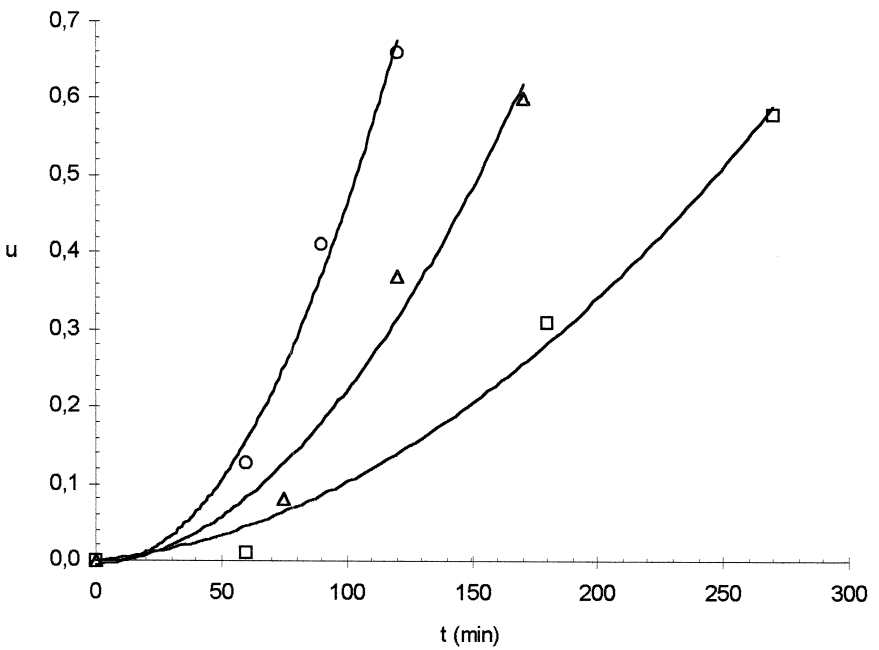


Fig. 4. Dimethoate conversion (u) in *quasi*-isothermal runs against time at different temperatures. (○) $T_1 = 393$ K, (Δ) $T_2 = 388$ K, (□) $T_3 = 383$ K, (—) Calculated conversion.

Table 1
Kinetic parameters obtained by fitting the data reported in Fig. 4 by using Eq. (2) and Fig. 3 by using Eqs. (3) and (4)

Parameter	Isothermal case	Adiabatic case
A (s^{-1})	$3.89\ 10^{+14}$	$3.89\ 10^{+14}$
E (kJ mol^{-1})	135	134
β	0.1310	0.1310

In order to study more accurately the kinetics, a set of runs has been performed in *quasi*-isothermal conditions. The results of experimental runs performed on samples of dimethoate at varying temperatures are reported in Fig. 4.

Experimental results point out that the decomposition process proceeds according to an auto-catalytic behaviour.

An attempt to model these data by means of a best fitting procedure allowed the identification of kinetic parameters, according to a simple auto-catalytic kinetic scheme:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

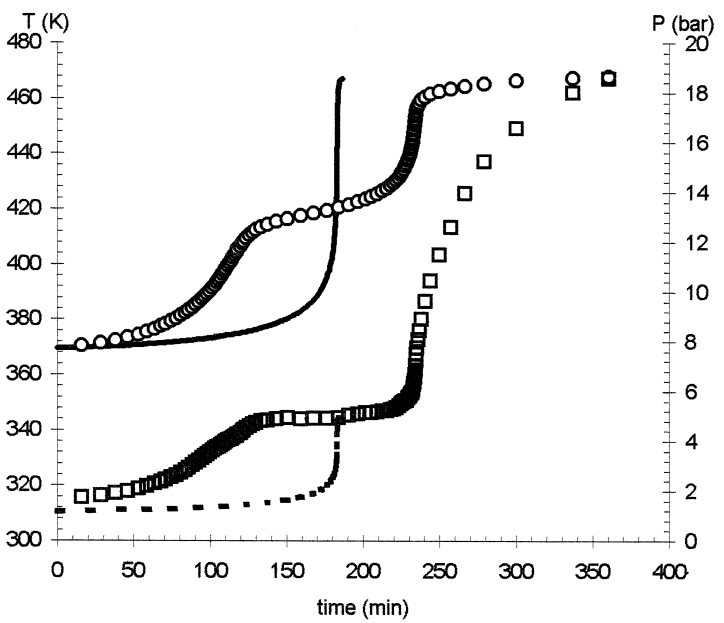


Fig. 5. Temperature and pressure plots vs. time during adiabatic A.R.C. run on a mixture of dimethoate/β-cyclodestrin hydrate in 1:1 weight ratio [Temperature (○); Pressure (□)] and pure dimethoate [Temperature (—); Pressure (—)].

By assuming an Arrhenius kinetics for the chosen scheme, the kinetic Eq. (2) can be written in the isothermal case and kinetic Eqs. (3) and (4) in the adiabatic case:

$$\frac{du}{dt} = k_2(1-u)(\beta+u) \tag{2}$$

$$\begin{cases} \dfrac{du}{dt} = Ae^{-\frac{E}{RT}}(1-u)(\beta+u) \end{cases} \tag{3}$$

$$\begin{cases} \dfrac{dT}{dt} = Ae^{-\frac{E}{RT}}(1-u)(\beta+u)\,\Delta T_{ad} \end{cases} \tag{4}$$

where β is defined as $\beta = k_{1/}k_2$, E is the activation energy, A the pre-exponential factor and R the gas constant. The results obtained by means of the identification procedure are reported in Table 1.

Table 2
(a) Decomposition products identified by means of GC-MS apparatus

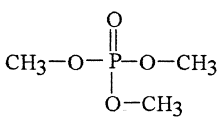
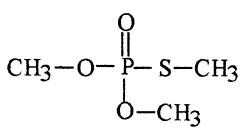
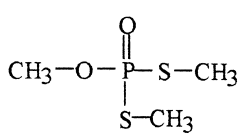
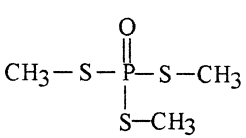
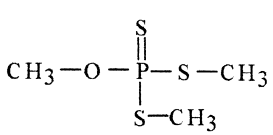
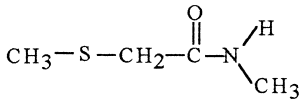
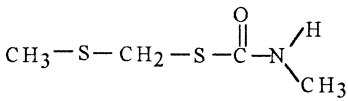
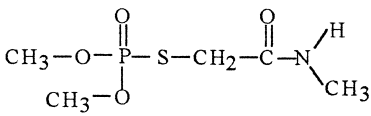
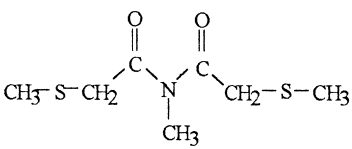
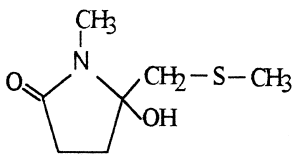
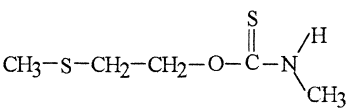
Structure formula	Chemical name	Fragmentation (m/e)
	*O,O,O*-phosphoric acid trimethyl ester (OOO)	140, 110, 95, 79, 55
	*O,O,S*-trimethylphosphoro-thioate (OOT)	156, 141, 126, 110, 95, 79, 58
	*O,S,S*-trimethylphosphoro-dithioate (OSTD)	172, 157, 125, 79
	*S,S,S*-trimethylphosphoro-trithioate (SSTT)	188, 173, 132, 101, 86, 55
	*O,S,S*-trimethylthiophosphoro-dithioate (OSTTD)	188, 173, 141, 108, 94, 79, 63

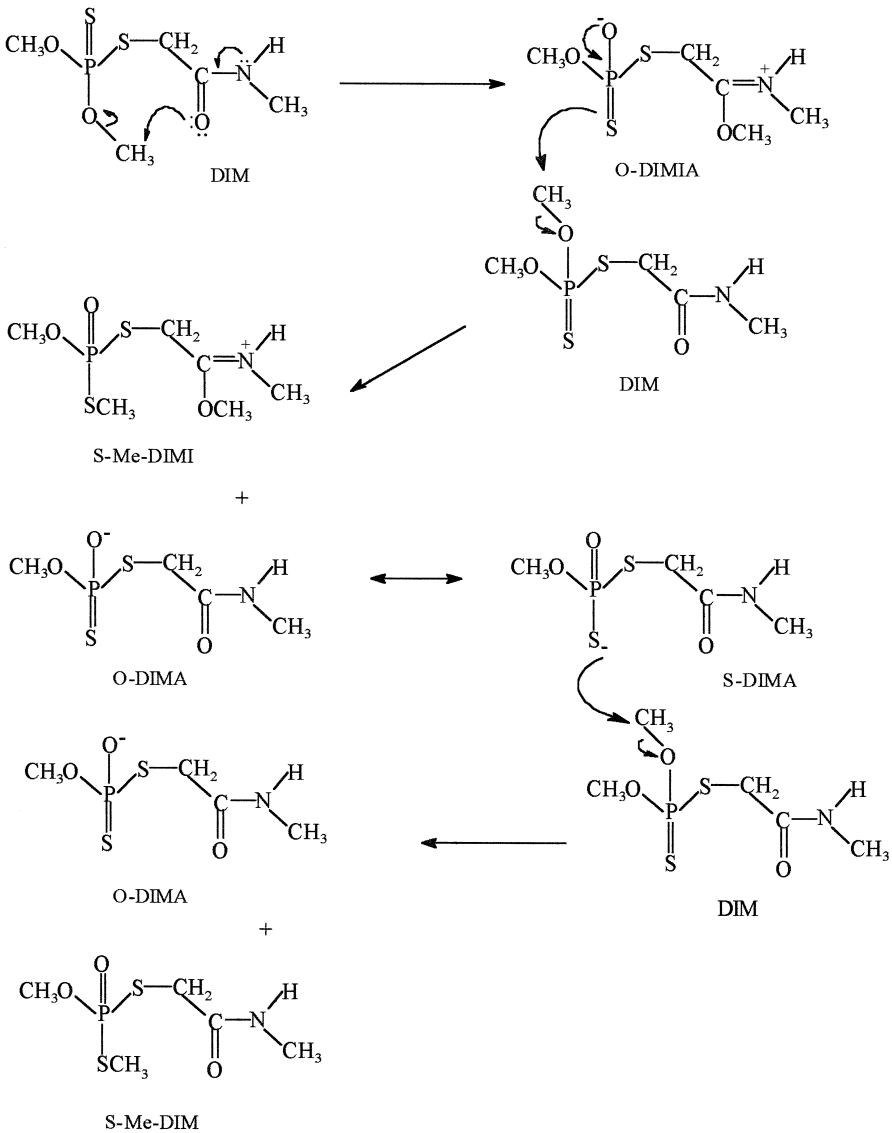
Table 2 (continued)
(b) Decomposition products identified by means of GC-MS apparatus

Structure formula	Chemical name	Fragmentation (m/e)
	2-*S*-methyl-(*N*-methyl) acetamide	119, 73, 58
	carbamothioic acid-(*N*-methyl)-*S*-methylthiomethyl ester	151, 121, 105, 93, 73, 61
	*O*,*O*-dimethyl-*S*-(*N*-methylcarbamoylmethyl) phosphorothioate (O-DIM)	214, 156, 141, 110, 79, 58
	*N*-methyl-2,2'-(*S*-methyl) diacetamide	207, 160, 146, 132, 118, 86, 61
	3-Hydroxy-4-*S*-methyl-(*N*-methyl) γ-valerolactam	175, 160, 132, 86, 61
	thiocarbamic acid-(*N*-methyl)-*O*-ethylthiomethyl ester	165, 135, 119, 91, 75, 61

Previous experiment by Maeda et al. [4] have shown that dimethoate stability is improved by the addition of β-cyclodextrin, provided an inclusion complex is formed.

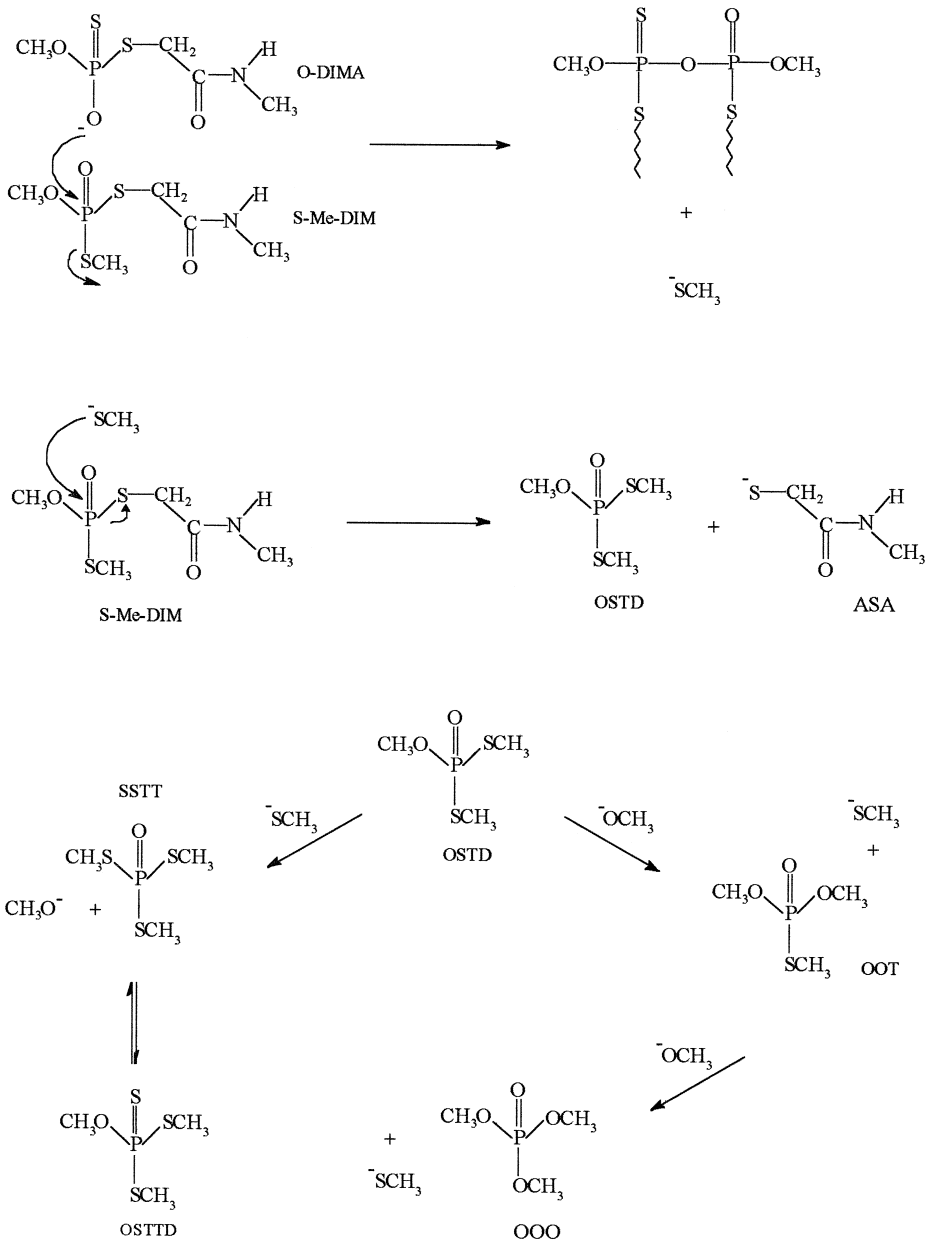
Although the single addition of β-cyclodextrin to dimethoate has been reported as ineffective [4], our experiments indicate that β-cyclodextrin hydrate (Cycloheptaamylose hydrate)/dimethoate mixtures (weight ratio 1:1) have a marked lower stability than pure dimethoate (Fig. 5).

As clearly pointed out by thermogram, the decomposition of the mixture starts at the same temperature ($T_o = 369$ K) as pure dimethoate (solid line) and exhibits a second exothermic event, probably due to β-cyclodextrin hydrate decomposition, with an experimental adiabatic temperature rise of $\Delta T_{ad,exp} = 98.4$ K that results in a real temperature rise of $\Delta T_{ad,real} = \Phi \cdot \Delta T_{ad,exp} = 255$ K. Although the starting temperature and Φ (2.6) are the same for the two systems (pure dimethoate and dimethoate/β-cyclodextrin hydrate), it is important to note that in the latter case a higher reactivity is



Scheme 1.

observed due to the reduced amount of the pesticide in the tested sample. This result suggests that an unexpected interaction between the two components occurs leading to a more reactive system.

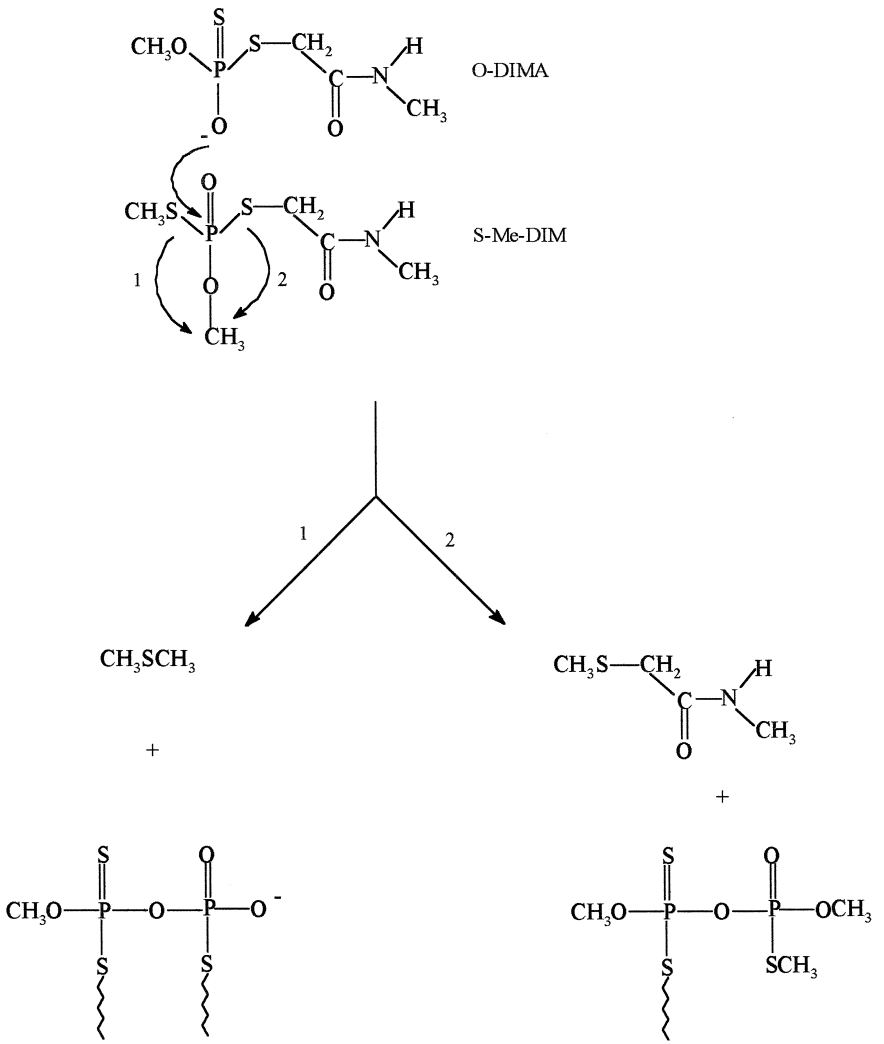


Scheme 2.

It is worth also to observe that a higher final pressure value ($P = 18.6$ bar) is achieved at the end of the decomposition for the system dimethoate/β-cyclodextrin hydrate.

A list of products identified by means of GC-MS analysis, performed on samples coming from a *quasi*-isothermal run and dissolved in methanol, is reported in the Table 2a and b.

Scant data are found in the literature about the toxicity of decomposition products (Lewis [5]). Some of these compounds, for example *O*,*O*,*O*-phosphoric acid trimethyl ester (OOO), are suspected carcinogen.



Scheme 3.

A possible explanation for the formation of the most part of them is given on the basis of the following remarks.

It has been reported in the literature that the isomerization of phosphorothionates compounds occurs on heating and is accelerated in presence of carboxylic acid amides (Maeda et al. [4], Eto et al. [6]).

Since an amidic center is present in the structure of DIM, the formation of *O*-methyl-*S*-methyl-*S*-(*N*-methylcarbamoylmethyl)phosphorothioate (*S*-methyl-dimethoate, *S*-Me-DIM) can be inferred. As indicated in Scheme 1, the isomerization could proceed through three steps.

According to Eto et al. [6] a direct attack of *S*-DIMA on *S*-Me-DIMI is ruled out from this scheme.

The presence of *S*-methyl phosphoric acid ester isomers (OSTD, SSTT, OOT, OSTTD) and of *O*,*O*,*O*-phosphoric acid trimethyl ester (OOO) among the reaction products can be well explained in Scheme 2 by means of a nucleophilic attack of *O*-DIMA anion on the phosphorus center of *S*-Me-DIM molecule (Patai [7]):

The nucleophilic attack of phosphorothionate anion (*O*-DIMA) on *S*-Me-DIM molecule could result also in the formation of 2-*S*-methyl-(*N*-methyl) acetamide or dimethylsulfide (Scheme 3). In the present work, only 2-*S*-methyl-(*N*-methyl) acetamide has been detected, whereas the presence of dimethylsulfide has been reported by Maeda [4].

Moreover, *S*-Me-DIM can undergo a nucleophilic attack by a free methoxy ion to give a *O*-DIM molecule, which is detected by GC-MS.

According to the literature (Patai [8]) in which it has been reported that the diamides can be converted to the corresponding imides by heating, the formation of *N*-methyl-2,2-(*S*-methyl) diacetamide can be explained as a result of the heating of the 2-*S*-methyl-(*N*-methyl) acetamide molecule.

4. Conclusions

The results of the investigation show that dimethoate can undergo a thermal decomposition process provided that the temperature is higher than 369 K. The decomposition process is characterized by a moderate autocatalytic behaviour (the degree of autocatalysis, β, is 0.1310). Many thiophosphoric toxic compounds have been identified among the decomposition products. A moderate increase of the system pressure has been recorded in all the runs.

Acknowledgements

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