Non-isothermal kinetic study of the thermal decomposition of N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide and N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide

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Abstract In this paper, the thermal behaviours of N-{bis[benzyl(methyl) amino]phosphoryl}-2,2-dichloro-acetamide (BMA) and N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA) were studied by thermo-gravimetery (TG) and differential scanning calorimetery (DSC) techniques under the non-isothermal conditions. The results showed that BMA melts about 120 °C before it decomposes. BMA decomposition occurs in three continuous steps, in the 170–400 °C temperature range. Each thermal degradation stage for BMA results an exothermic peak in the DSC curve. On the other hand, applying TG-DSC techniques indicates that DBA melts about 175 °C before it decomposes. This compound decomposes in the temperature range of 200–600 °C in three steps. Activation energy and pre-exponential factor for each compound were found by means of Kissinger method and were verified by Ozawa–Flynn–Wall method. Activation energy obtained by Kissinger method for the first stage of BMA and DBA decompositions are 151.8 ($\pm$2.0) KJ mol^{-1} and 138.7 ($\pm$2.6) KJ mol^{-1}, respectively. Finally, the thermodynamic parameters ($\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$) for first step decomposition of DBA and BMA were determined.

Keywords Organophosphorus compounds · Thermal stability · Non-isothermal · Activation energy · DSC · TG/DTA · Ozawa · Thermodynamic properties

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Introduction

Organophosphorus compounds (OPs) have extensively usage as insecticides in agriculture. They are known to modulate their biological effects through the inhibition of a number of esterase including acetylcholinesterase (AChE), the enzyme responsible for the degradation of the neuro-transmitter acethylcholine [1]. Their inhibitory effect is based on phosphorylation of serine hydroxyl group at the esteratic site of the enzyme active site [2]. The main mode of action of the OPs is inhibition of acetylcholinesterase, the enzyme that terminates the action of acetylcholine neurotransmitter, which is released by nerve stimulation, on postsynaptic cholinergic receptors in the nervous system. OPs produce an irreversible inhibition of acetycholinesterase, in contrast to the carbamates (the second major class) that produce a reversible inhibition [3, 4].

The widespread use of organophosphorus pesticides throughout the agricultural industry has resulted in mixed impacts. On one hand, utilization of pesticides produces an enormous increase in agricultural productivity. On the other hand, because of their hazardous nature, the wastes and reinstates from spray and storage equipment have been sources of surface water and ground water contamination. Therefore, pesticide reinstate depicts one of the major threats for the environment. Their occurrence has given rise

to a challenging natural resources management problem and, at the same time, has provided a source of motivation for many scientific initiatives. Many studies have been published, most of which are devoted to the metabolism and toxicity of these pesticides in mammals [5–7]. An understanding of their degradation in the environment is significant in predicting their fate after application.
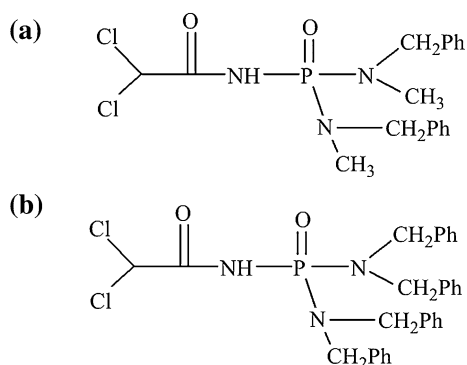
N-{bis[benzyl(methyl) amino]phosphoryl}-2,2-dichloroacetamide (BMA) and N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA), with the structures shown in Fig. 1, are two relatively new synthesized OPs; and hence, acquiring information concerning these compounds in the solid-state, including their thermal stability and thermal decomposition is necessary. This study is designed to investigate thermal stability of these organophosphorous compounds by means of differential scanning calorimetery (DSC) and simultaneous thermogravimetery-differential thermal analysis (TG-DTA). Also, this study seeks for determination of kinetic parameters of non-isothermal decomposition of the compounds.

Thermal stability studies of different materials by DSC, DTA and TG have been carried out for several years [8–11]. Kinetic studies have become a crucial point in thermal analysis, in which the main purpose is to determine the mechanism of pyrolysis reaction and to calculate the parameters of the Arrhenius equation [12–15]. To the best of our knowledge, there is no report on the thermal behaviour of these compounds.

Experimental

Synthesis procedure

N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) was synthesized via the reaction of $Cl_2C(O)$ $NHP(O)Cl_2$ with methylbenzylamine in a 1:4 molar ratio.

Fig. 1 Chemical structural of investigated organophosphorous compounds **a** N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and **b** N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA)

Metylbenzylamine was added dropwise to a mixture of $Cl_2C(O)NHP(O)Cl_2$ in chloroform while stirring at room temperature for 2 h. The product was filtered off and then washed with cold water. The compound was recrystallized from ethanol (yield 88%). Analysis, calculated for $C18H22Cl2N3O2P$: C 52.19, H 5.35, N 10.14%; found: C 52.18, H 5.36, N 10.15%.

N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA) was synthesized via the reaction of $Cl_2C(O)NHP(O)Cl_2$ with dibenzylamine in a 1:4 molar ratio. Metylbenzylamine was added dropwise to a mixture of $Cl_2C(O)NHP(O)Cl_2$ in chloroform while stirring at room temperature for 4 h. The product was filtered off and then washed with cold water. The compound was recrystallized from ethanol (yield 88%). Analysis, calculated for $C30H30Cl2N3O2P$: C 63.61, H 5.34, N 7.42%; found: C 63.62, H 5.35, N 7.41%.

Thermal characterization

Differential scanning calorimetery experiments were conducted using the DuPont Instrument Model DSC 910S differential scanning calorimeter. Aluminum crucibles containing the samples were purged with nitrogen at a flow rate of 50 mL min^{-1}. The DSC experiments were carried out in a scanning mode at heating rates of 5, 10, 15 and 20 °C min^{-1} in the temperature rang of 25–700 °C. The instrument was calibrated at each heating rate considered using a dedicated 1 mg indium standard in an aluminum pan. Plotting for exothermic reactions was as down ward deflection of the curve peak from the baseline.

Thermogravimetery (TG) analysis was carried out using a Stanton Redcroft, STA-625 series with alumina crucibles; with a heating rate of 10 °C min^{-1} in a temperature range of 50–700 °C, under nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The sample mass was about 5 mg.

Results and discussion

The TG and DSC curves at a heating rate of 10 °C/min for both compounds are given in Fig. 1. As shown in Fig. 1a for BMA, melting occurs at 120 °C during an endothermic phenomenon. No change in the mass of compound was observed until 150 °C. Above this temperature, three continuous exothermic peaks occurred with a major fall in the sample's mass until about 400 °C. During these three steps, TG curve indicate a continuous mass loss that it continued up to 400 °C. The results indicated a mass loss in TG curve about 82% for these three steps.

Figure 1b shows DSC and TG curves of DBA. As shown in this figure, melting occurs at 175 °C during an endothermic phenomenon and as seen in TG curve of DBA, up to 228 °C, no change in the mass of the

Table 1 Summary of TG/DSC results

Component	Transition temperature/°C			Mass loss/%
	Melting	Decomposition	T^*	
BMA	120	219	170–400 (decrease)	82
DBA	175	228	200–600 (decrease)	95

* T is the temperature when there is fall in a sample's mass

Fig. 2 TG/DSC curves for **a** N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and **b** N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA); sample mass 5 mg; heating rate 10 °C min⁻¹

compound was observed. A violent decomposition happened, above this temperature and TG curve showed strong mass loss after this temperature. The decomposition took place in three steps. These steps are consecutive exothermic decomposition processes. A total mass loss observed in TG curve was about 95%.

The general information about thermal behaviour of BMA and DBA compounds in terms of stability range, peak temperature and percentage of mass loss corresponding to each compound is presented in Table 1.

Effect of heating rate

Figure 2 shows DSC curves for BMA and DBA at several heating rates. The data presented in this figure shows that as the heating rate was increased, the melting peak of the compounds was shifted to higher temperatures. These shifts in melting point are shown in Table 2 and Fig. 3. On the other hand as shown in Table 2 and Fig. 3, there was an increase in the temperature of the decomposition peaks of both compounds as the heating rate increased.

Thermal decomposition kinetics

In view general complexity in the processes involved in solid-state reactions, [16–19], two thermal analysis kinetic methods were jointly employed in this study to process the DSC data to calculate the Arrhenius parameters, such as the activation energy (E) and the pre-exponential factor (A) for the both compounds studied. These methods are as follows:
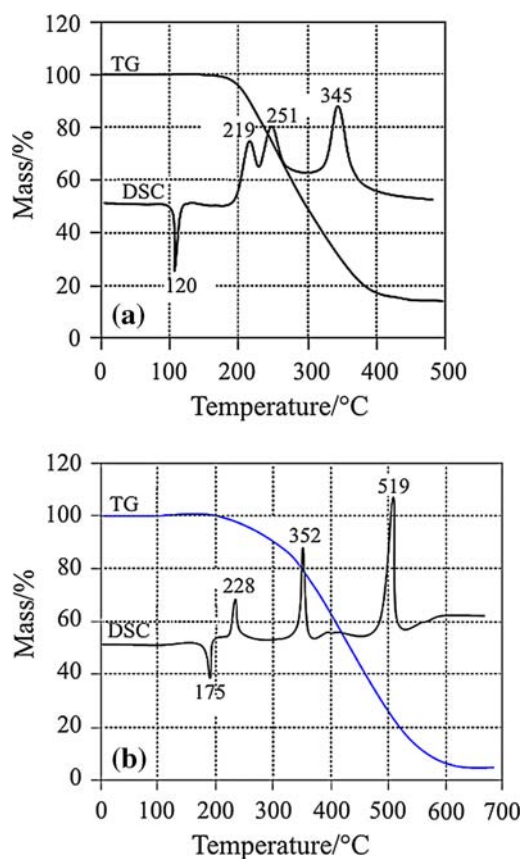
Kissinger equation [16]:

$$\ln \frac{\phi}{T_{\mathrm{m}}^2} = \ln \frac{AR}{E} - \frac{E}{RT_{\mathrm{m}}} \tag{1}$$

where, ϕ is heating rate, T_{m} maximum peak temperature, and R the gas constant.

Ozawa–Flynn–Wall equation [20]:

$$\log \phi = \log \frac{AE}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E}{RT_{\mathrm{m}}} \tag{2}$$

where, $g(\alpha)$ is the integral function of conversion. This equation is valid in the range $20 < X = E/RT < 60$ (Doyle's approximation), which in our study, the x factor for both compounds was in this range.

These multiple scanning methods are model free isoconventional methods and allow the activation energy to be independently obtained [21]. The E values calculated using each method was used to check the constancy and validity of activation energy obtained by another method.

On the other hand, the Arrhenius pre-exponential factor (A) was found for both compounds from the following relation [22, 23]: $A = \phi E \exp (E/RT_{\mathrm{m}})/RT_{\mathrm{m}}^2$.

The values of activation energy and pre-exponential factor of decomposition calculated by the Kissinger method and those calculated according to the Ozawa–Flynn–Wall method have been compared (Table 3). As could be found in this table, the activation energies and pre-exponential factors calculated by Kissinger method for both compounds were comparable with which obtained by Ozawa–Flynn–Wall method.

Table 2 Melting point and decomposition temperature of N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA) obtained by DSC at various heating rate

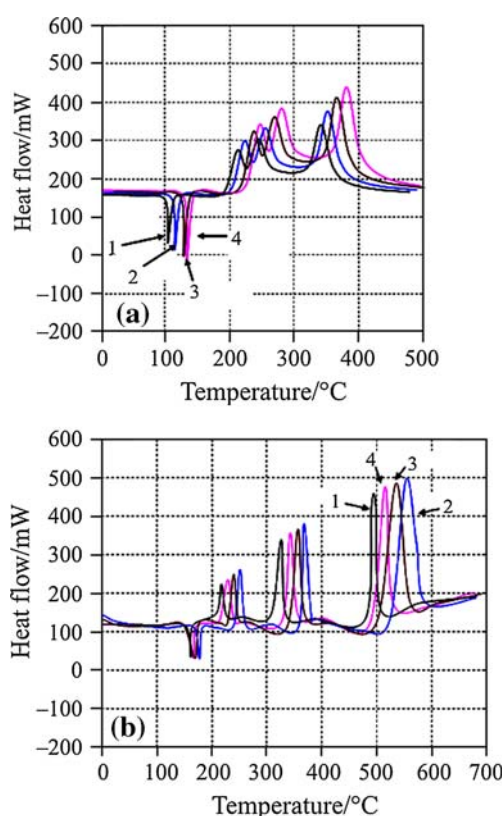| Compound	BMA				DBA			
Heat flow/ °C min^{-1}	Melting point/°C	Decomposition temperature/°C			Melting point/°C	Decomposition temperature/°C		
		Step 1	Step 2	Step 3		Step 1	Step 2	Step 3
5	120	212	240	310	175	220	335	501
10	122	219	251	325	176	228	352	519
15	125	226	271	345	177	235	365	533
20	127	229	275	390	179	240	382	565

After the kinetic parameters, E and A were obtained, the thermodynamic parameters of activation can be calculated from the following equations [24, 25]:

$$A \exp \frac{-E}{RT} = v \exp \frac{-\Delta G^{\#}}{RT} \tag{3}$$

$$\Delta H^{\#} = E - RT \tag{4}$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{5}$$

where, $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ are free energy, enthalpy and entropy of the activation, respectively. v is the $v = K_B T/h$ (where K_B and h are Boltzmann and Plank constant, respectively). Tables 3 and 4 give the computed thermodynamic and kinetic parameters for both compounds studied. Based on the kinetic data, activation energy of BMA is approximately 13 kJ mol^{-1} higher than DBA, and hence, the relative stability of these organophosphorous compounds was found to obey in this order: BMA > DBA. This trend could be seen in calculated reaction rate constants (k), BMA ($k = 2.4 \times 10^{-9}$), DBA ($k = 6.2 \times 10^{-9}$). It is obvious that the reaction rate constant of BMA is lower than that calculated for the DBA. Also, same trend could be seen in values of thermodynamic parameters ($\Delta H^{\#}$, $\Delta G^{\#}$) calculated for both organophosphorous compounds [26]. These results could be used in the environmental science for prediction the lifetime (in the identical condition BMA has approximately three times longer half-life than DBA). Also, these data can provide valuable information about time and condition of storage.

Critical thermal explosion temperature

The critical explosion temperature (T_b) an important parameter required to insure safe storage and process operations involving organic and inorganic materials. It is defined as the lowest temperature to which a specific charge may be heated without undergoing thermal runaway

Fig. 3 The effect of heating rate on the melting point and decomposition temperature of **a** N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and **b** N-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA); sample mass 5 mg; nitrogen atmosphere

Table 3 Comparison of kinetic parameters of the N-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) obtained by Kissinger and Ozawa–Flynn–Wall methods

Method	E/KJ mol^{-1}	Log Z/A/s^{-1}	Correlation coefficient	$\Delta G^{\#}$/KJ mol^{-1}	$\Delta H^{\#}$/KJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1}	$T_{1/2}$/year	T_b/°C
Kissinger	151.8 (±2.0)	15.9	0.9934	124.13	147.66	49	9.1	222.4
Ozawa	151.8 (±2.3)	16.0	0.9942	124.08	147.72	48	9.0	222.4

Table 4 Comparison of kinetic parameters of the *N*-{bis[dibenzylamino]phosphoryl}-2,2 dichloroacetamide (DBA) obtained by Kissinger and Ozawa–Flynn–Wall methods

| Method	E/KJmol^{-1}	Log Z/ A/s^{-1}	Correlation coefficient	$\Delta G^{\#}$/ KJ mol^{-1}	$\Delta H^{\#}$/ KJ mol^{-1}	$\Delta S^{\#}$/ J mol^{-1}	$T_{1/2}$/ year	T_b/ °C
Kissinger	138.7 (±2.6)	14.2	0.992	126.9	134.13	14	3.51	227.0
Ozawa	137.3 (±3.0)	14.1	0.9948	127.0	133.13	12	2.95	227.1

[27–29]. T_b may be calculated from inflammation theory and appropriate thermokinetic parameters namely the activation energy, pre-exponential factor, and heat of reaction. In order to obtain the critical temperature of thermal explosion (T_b) for these compounds, Eqs. 3 and 4 were used [30].

$$T_e = T_{e0} + b\phi_i + c\phi_i^2, \quad i = 1-4 \tag{6}$$

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{e0}}}{2R} \tag{7}$$

where b and c are coefficients, R is the gas constant; E is the value of activation energy obtained by kinetic method.

The value (T_{e0}) of the onset temperature (T_e) corresponding to $\phi \rightarrow 0$ obtained by Eq. 3 is 209 and 212 °C for BMA and DBA, respectively.
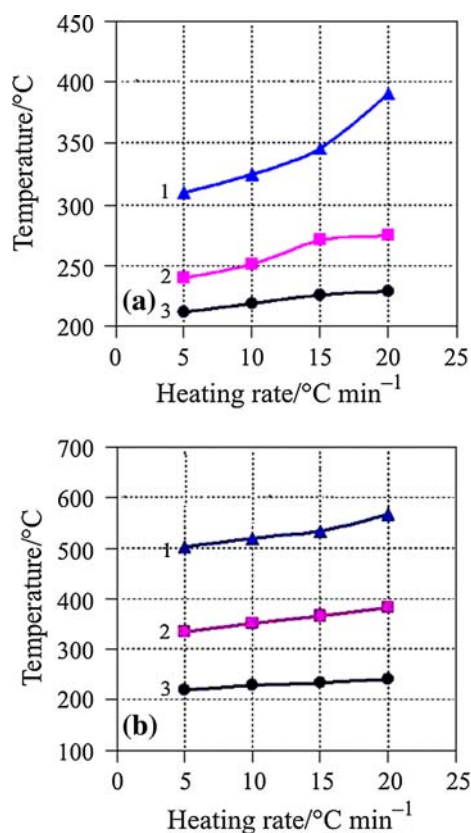
Fig. 4 The effect of heating rate on the melting point and decomposition temperature of **a** *N*-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and **b** *N*-{bis[dibenzylamino]phosphoryl}-2,2-dichloroacetamide (DBA) obtained by DSC

The critical temperature of thermal explosion (T_b) obtained from Eq. 4 for each compounds by using ASTM and Ozawa data are is shown in Tables 3 and 4.

Conclusions

The thermal behaviour of two Organophosphorus (OP) componds, *N*-{bis[benzyl(methyl)amino]phosphoryl}-2,2-dichloroacetamide (BMA) and *N*-{bis[dibenzylamino] phosphoryl}-2,2-dichloroacetamide (DBA), was studied using TG and DSC. The results showed that BMA and DBA were melted at about 120 and 175 °C, respectively, before they decompose. On the other hand, both compounds showed that their mass losses are consecutive and there no plateaus in the decomposition temperature interval in the TG curve (Fig. 4).

The values of the kinetic parameters that were obtained by the Kissinger and Ozawa–Flynn–Wall methods for BMA and DBA showed good correlation, but the values of activation energy and frequency factor obtained by Kissinger method were comparable with those obtained by Ozawa–Flynn–Wall method. On the other hand, the values of $\Delta S^{\#}$, $\Delta G^{\#}$ and $\Delta H^{\#}$ of the first stage of decomposition reaction of BMA and DBA were computed. Our finding showed that, the values of the $\Delta G^{\#}$ for the decomposition of BMA and DBA are comparable. But, the values of the activation enthalpies ($\Delta H^{\#}$) and activation entropies ($\Delta S^{\#}$) for the decomposition of BMA are considerably higher and lower than decomposition of DBA, respectively.

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