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# Effect of malonyl malonanilide dimers on the thermal stability of nitrocellulose

M.A. Hassan\*

*Fire and Explosion Protection Department, National Institute for Standards,  
P.O. Box 136, Code 12211 Giza, Egypt*

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## Abstract

Three malonanilide dimers (MA2–MA4) were prepared by the reaction of ethyl malonate with malonanilide derivatives (M2–M4). These dimers were investigated as new stabilizers for nitrocellulose. The evaluation process has been performed through Bergman–Junk (BJ) test, thermal analysis measurements (TGA and DSC) and kinetic parameters calculations ( $E_a$ ). The comparative study between mass spectra and thermal analysis of the new dimers helped in resolving the thermal decomposition mechanisms for the new dimers. It was found that the new dimers especially (MA2 and MA4) showed better stabilizing effect for the nitrocellulose than the centralite 1 (C1) which is the common stabilizer. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Nitrocellulose; Stabilizers; Malonanilides; Thermal analysis; Stability test; Kinetic analysis

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## 1. Introduction

Nitrocellulose, is used as the main constituent in propellants. During the storage of nitrocellulose,  $\text{NO}_2$  is liberated which reacts with water forming acid. If nitrogen oxide gases are not removed, they accelerate the nitric acid esters degradation, shorten, therefore, the service life time and heat is produced as a consequence, self ignition may occur by accelerated decomposition caused by auto catalysis or by self heating and several disasters throughout the world bear witness to this. To remedy this situation, stabilizers like diphenylamine and ethylcentralite are added to gun and rocket propellants formulations. These stabilizers react easily with nitrogen oxides and prevent the auto catalytic decomposition of propellants. The reaction of these compounds are complex and many consecutive products of the primary stabilizer, also named daughter products are formed.

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\* Fax: +20-386-7451.

E-mail address: m.aly@sit.nis.sci.eg (M.A. Hassan).

Different classes of organic compounds like amines, amides, heterocyclic compounds which are based on imidazole and pyrazole have been long recognized as stabilizers for propellants [1–6]. Recently, some of malonanilide derivatives showed good results as stabilizers for double base propellants [7]. These results were the drive to synthesis new malonanilide dimers and to study the effect of changing the structure on their properties as stabilizers for propellants. The evaluation of propellant stabilizers depends on the thermal stability test [8] and also on the thermal analysis techniques [9–11]. Thermal analysis study of energetic materials is important not only for understanding of the kinetics of their thermal decomposition but also for assessing the effect of their exothermic decomposition on the potential hazardous in their handling, processing and storage. Kinetic studies also provide useful information on thermal stability and life expectancy ( reliability ) of the energetic materials under different thermal environment at storage. The thermo analytical methods usually employed for the study of thermal decomposition of energetic materials ( like propellants and propellants ingredients ) are thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimeter (DSC).

Zayed and Nour El-Dien [12,13] have made a comparative study between the thermal analysis (TGA and DSC) and mass spectra of some complexes to highlight the thermal decomposition mechanism of these complexes. The same technique will be used to predict the thermal decomposition mechanism of the stabilizers under investigation.

The aim of the present work in this paper, is to synthesis new malonanilide dimers and to study the effect of changing their structure on their properties as stabilizers for propellants. The results are compared with the classical stabilizer centralite 1 (C1).

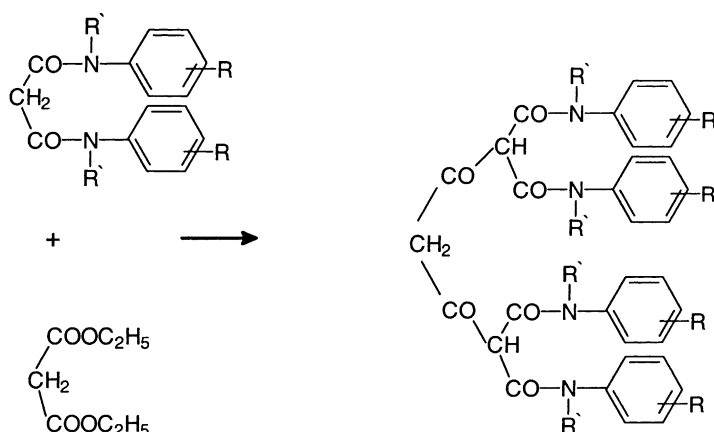
## 2. Experimental

The chemicals used in the preparation of malonanilide dimers are diethylmalonate, *N*-ethyl aniline, *o*-nitro aniline and *p*-nitro aniline of purity 98% and produced by Merck and Aldrich. Malonanilide dimers (MA2–MA4) were prepared by condensation reaction of malonanilides (M1–M3) with diethylmalonate according to Chattway method [14].

Nitrocellulose (12.02 N%) was mixed by solvent less method with malonanilide dimers (3%), dibutylphthalate (4%) and transformer oil (1%).

The Bergman–Junk ( BJ ) test at was carried out at 132°C for 2 h using 1 g. In this test, nitrocellulose samples were heated in BJ bath for 2 h at 132°C and after that 50 ml distilled water were mixed with the nitrocellulose samples and shaken well. The 25 ml of this water sample were titrated against 0.05 N NaOH using methyl red as indicator.

For non-isothermal and isothermal analysis ( 80, 120 and 150°C ) TGA and DSC of Shimadzu-50 were used to study the decomposition of nitrocellulose samples containing malonanilides dimers and C1. In the TGA test, the weight loss percentage is measured against the desired temperature and in DSC test, the changes in H of the tested sample is measured against temperature. All the thermal analysis experiments were carried out using 3–5 mg samples under inert nitrogen atmosphere with heating rate 10°C min<sup>-1</sup>.



MA2 = malonyl *p,p'*-dinitromalonanilide, dimer  $R' = H$ ,  $R = p\text{-NO}_2$

MA3 = malonyl *N,N'*-diethylmalonanilide dimer  $R' = C_2H_5$ ,  $R = H$

MA4 = malonyl *o,o'*-dinitromalonanilide dimer  $R' = H$ ,  $R = o\text{-NO}_2$

### 3. Results and discussion

The evaluation of the new malonanilide dimers (MA2–MA4) as new stabilizers depends on the comparison with the classical stabilizer C1. The BJ test has been chosen to evaluate the effect of the new stabilizer on the thermal stability of nitrocellulose as it is the most widely used quantitative stability test. The results of BJ test of the nitrocellulose samples containing the two dimers (malonyl *o,o'*-dinitromalonanilide (MA4) and malonyl *p,p'*-dinitromalonanilide dimers) show that they have higher thermal stability (0.6 and 0.7 ml of NaOH equivalent to nitric oxide gases dissolved in water) than nitrocellulose samples containing the classical stabilizer (0.8 ml) while nitrocellulose samples containing the malonyl *N,N'*-diethylmalonanilide dimer have a little bit lower thermal stability (0.9 ml) in comparison with the classical stabilizer, see Table 1.

The results of non-isothermal TGA show that the new malonanilide dimers gave the nitrocellulose higher DTG peaks (MA4 = 307°C, MA2 = 290.4°C and MA3 = 269°C) in comparison with the classical stabilizer (C1 = 266°C). Also the time difference between starting decomposition and reaching the DTG peak temperatures are bigger in case of nitrocellulose samples containing the new dimers (MA2 = 10.67 min, MA3 = 10.86 min

Table 1  
The Bergmann and Junk results of the nitrocellulose containing different stabilizers

Stabilizers	BJ at 132°C of NaOH (ml)
C1	0.8
MA2	0.7
MA3	0.9
MA4	0.6

Table 2

Decomposition temperatures of nitrocellulose sample containing different stabilizers

Stabilizers	Temperature of starting decomposition (°C)	DTG peak temperature (°C)	Time difference between starting decomposition and DTG peak (min)
C1	170	266	9.46
MA2	189	290.4	10.67
MA3	173	269	10.86
MA4	193	307	11.42

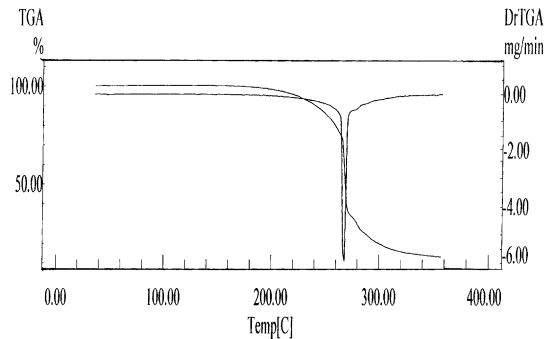


Fig. 1. TGA and DrTGA of nitrocellulose containing C1.

and MA4 = 11.42 min) than that containing the classical one (9.46 min), see Table 2 and Figs. 1 and 2.

The results of the isothermal TGA at 80, 120 and 150°C show that the weight loss percentage of the nitrocellulose samples containing the new dimers are lower than that containing the classical stabilizer (see Table 3). The samples containing the MA4 dimer show the lowest weight percentage among the different stabilizers under investigations at

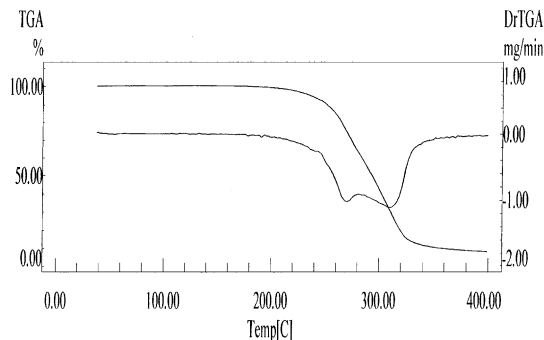


Fig. 2. TGA and DrTGA of nitrocellulose containing MA4.

Table 3

Isothermal TGA of the nitrocellulose samples containing different stabilizers

Stabilizers	Isothermal temperatures (°C)		
	80	120	150
Weight loss (%)			
C1	0.177	1.474	6.485
MA2	0.173	1.452	5.707
MA3	0.187	1.1122	5.747
MA4	0.143	0.920	5.436

Table 4

DSC results of nitrocellulose samples containing different stabilizers with correlation of TG losses within the decomposition range ( $T_i-T_f$ )

Stabilizers	$T_i$	$T_m$	$T_f$	Weight loss (%)
C1	171.89	198.63	268.84	62.79
MA2	171.08	197.07	243.58	11.20
MA3	169.45	199.03	268.02	36.29
MA4	167.01	197.40	250.92	10.21

different temperatures (0.14, 0.92 and 5.44%). The corresponding weight loss percentage of the other dimers and the classical stabilizer are as follow (MA2 = 0.17, 1.46, 5.71%, MA3 = 0.19, 1.11, 5.75% and C1 = 0.177, 1.474, 6.485%). The above results indicate that the new dimer MA4 increases the thermal stability of the nitrocellulose by about 16% at different temperatures more than the classical one, while the dimers MA2 and MA3 increase the thermal stability by 12, 11.4% more than the classical stabilizer.

The results of TGA of nitrocellulose samples containing different stabilizers under investigation within the decomposition range (DSC results) are given in Table 4 and are shown in Figs. 3 and 4. It was found that in general the nitrocellulose samples containing the new dimers have a lower value of weight loss percentage within the decomposition range in comparison with the classical stabilizer. The nitrocellulose samples containing the MA4

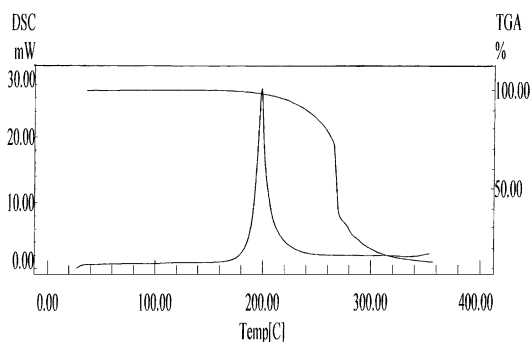


Fig. 3. The relation between TGA and DSC results of nitrocellulose containing C1.

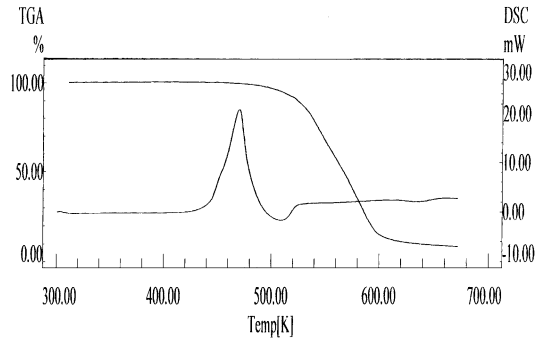
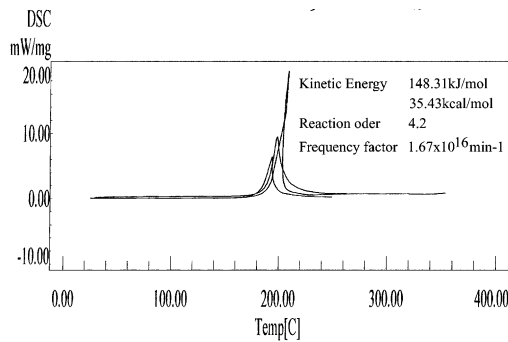


Fig. 4. The relation between TGA and DSC results of nitrocellulose containing MA4.

Table 5

Kinetic parameters of the thermal decomposition of nitrocellulose samples containing different stabilizers

Stabilizers	$E_a$ (kJ mol <sup>-1</sup> )	Reaction order	Frequency factor
C1	148.31	4.2	$1.67 \times 10^{16}$
MA2	157.20	1.2	$2.24 \times 10^{17}$
MA3	146.69	3.1	$1.30 \times 10^{16}$
MA4	161.03	1.4	$6.52 \times 10^{17}$



LOG A

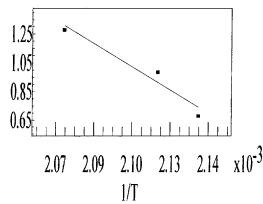


Fig. 5. The Ozawa plot of nitrocellulose containing C1.

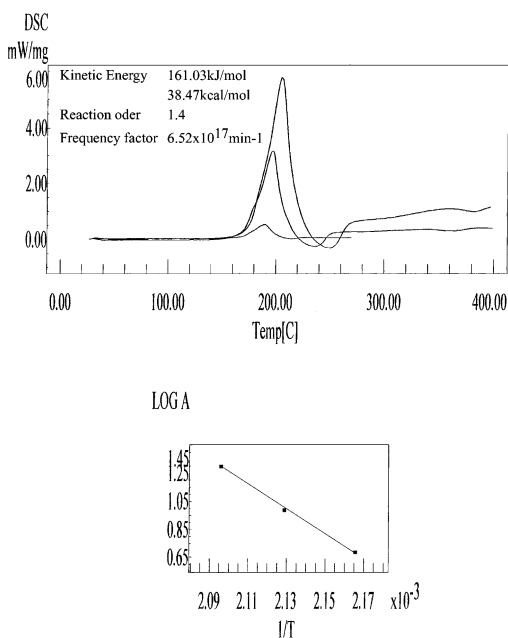


Fig. 6. The Ozawa plot of nitrocellulose containing MA4.

dimer lost 10.21% of its weight within the decomposition range (167.01–250°C). This is the best result achieved by the new dimers. The nitrocellulose sample containing the MA2 dimer lost 11.20% of its weight within the decomposition range (171.08–243.85°C), while the nitrocellulose sample containing the third dimer MA3 lost 36.29% of its weight. On the other hand, we can see the big difference in weight loss between the nitrocellulose samples containing the new dimers and that ones containing the classical stabilizer (62.79%) within the decomposition range. These results demonstrate that the new dimers are efficient as good stabilizers for propellants.

The results of kinetic parameters calculation by Ozawa method [15] are given in Table 5 and Figs. 5 and 6. The order of increasing the activation energy of decomposition of nitrocellulose samples containing different stabilizers are as follow:

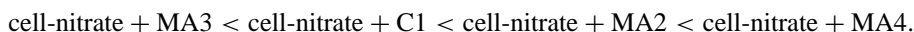


Fig. 7 represents the TGA and DSC curves of malonyl *p,p'*-dinitromalonanilide dimer within the temperature range 20–700°C. The TGA curve shows two-steps of mass losses of 80%. The first-step of mass loss (3.88%) occurs within the temperature range 90–100°C and may accounts for moisture release. The main mass loss is 76.12% occurs within the temperature range 265.17–700°C which accounts for the losses of NO<sub>2</sub>, NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, CO, CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> groups after fragmentation of the compound. The DSC curve of MA2 indicates the appearance of three endothermic and one exothermic peaks. The first endothermic peak is centered at 91°C which may be related to the moisture release.

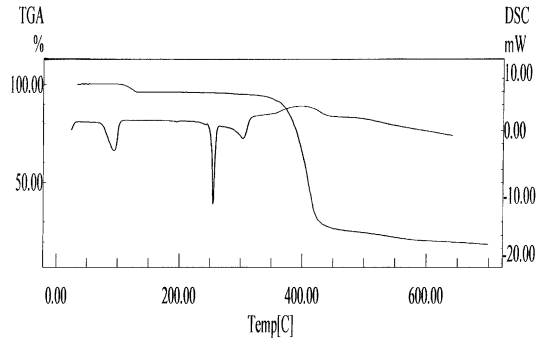
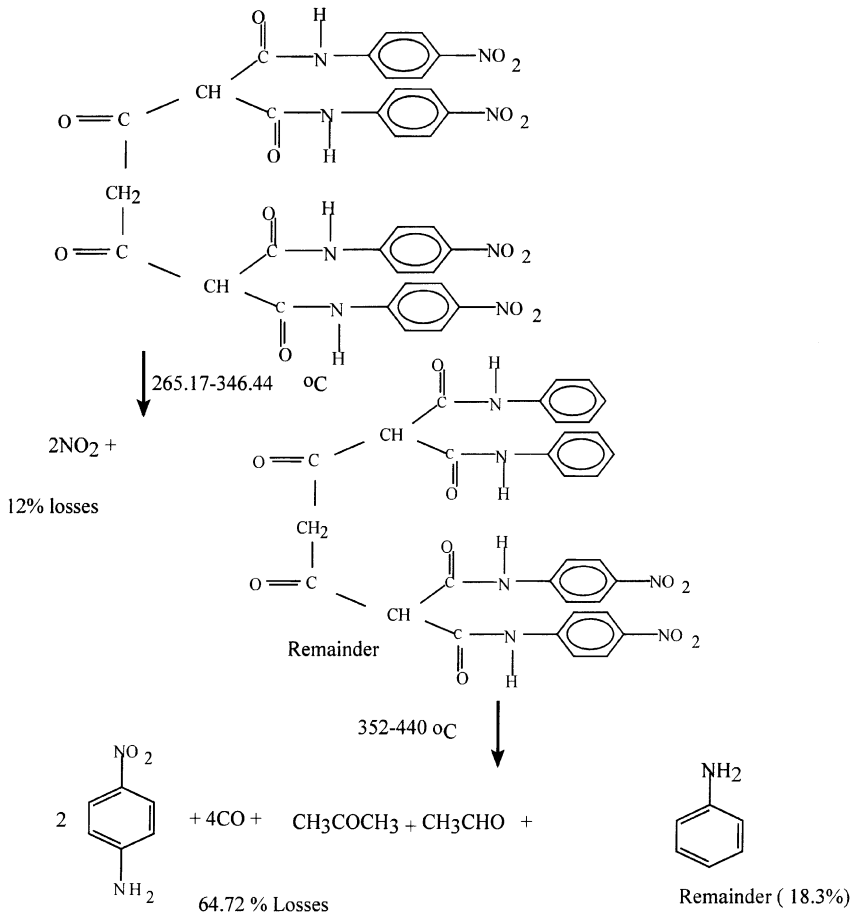


Fig. 7. TGA and DSC of MA2.



Scheme 1.



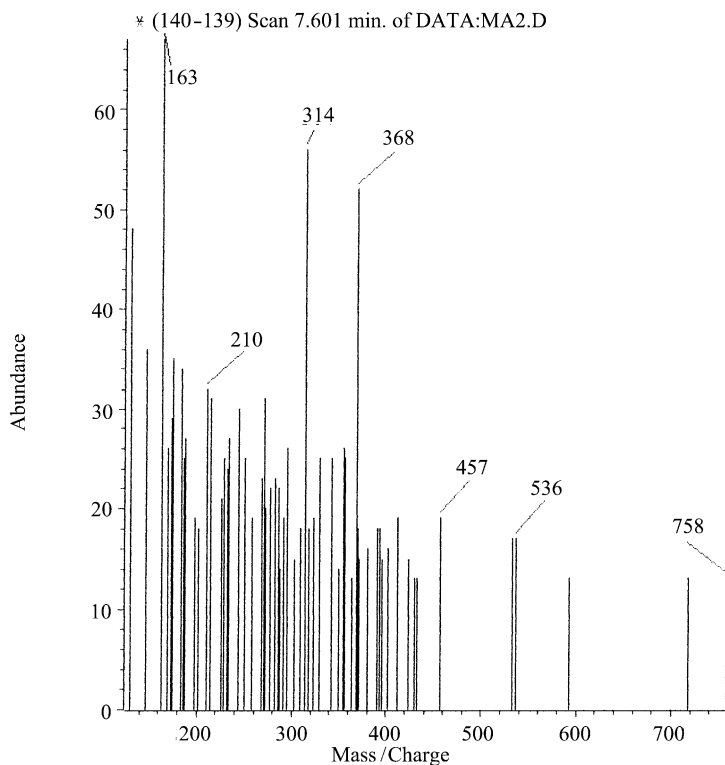


Fig. 8. Mass spectrum of MA2.

The second sharp one at 259.64°C is related to the melting point of the compound. The third endothermic peak (265.17–346.44°C) and the fourth exothermic one (352–440°C) are related to the thermal decomposition of the compound. The thermal analysis scheme of decomposition of MA2 dimer is as shown in Scheme 1.

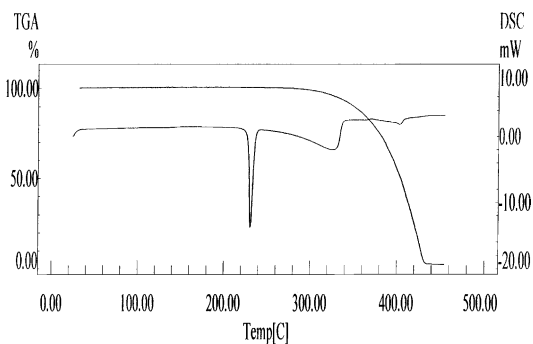
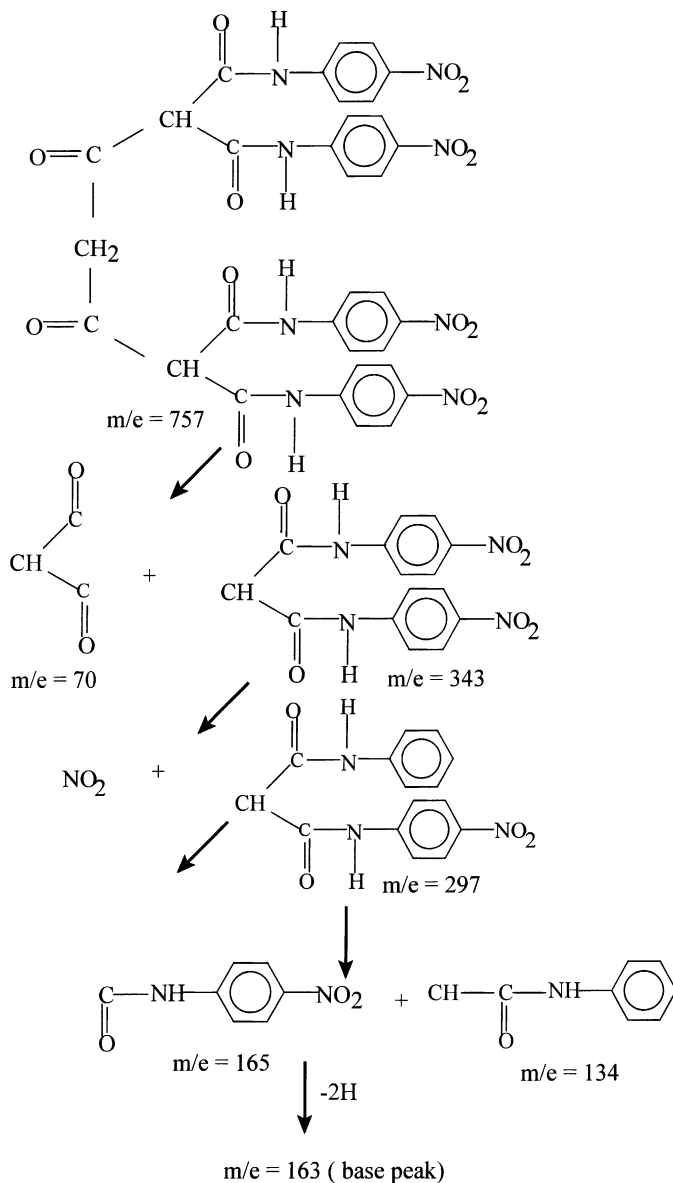


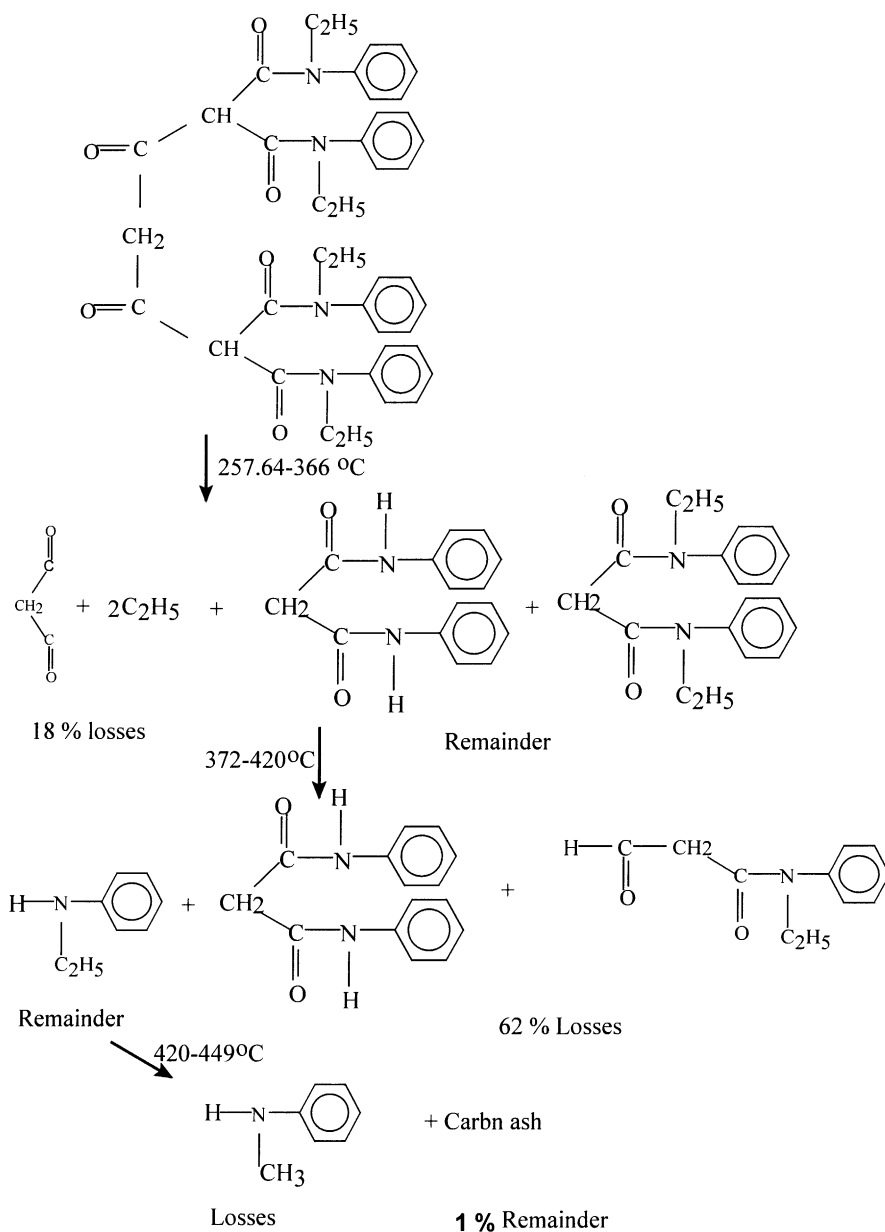
Fig. 9. TGA and DSC of MA3.

The recorded mass spectra of MA2 is given in Fig. 8, from this spectrum the fragmentation pattern can be represented by the Scheme 2.

Fig. 9 represents the TGA and DSC curves of malonyl *N,N'*-diethylmalonanilide dimer within the temperature range 20–450°C. The TGA curve shows one-step mass loss of



Scheme 2.



Scheme 3.

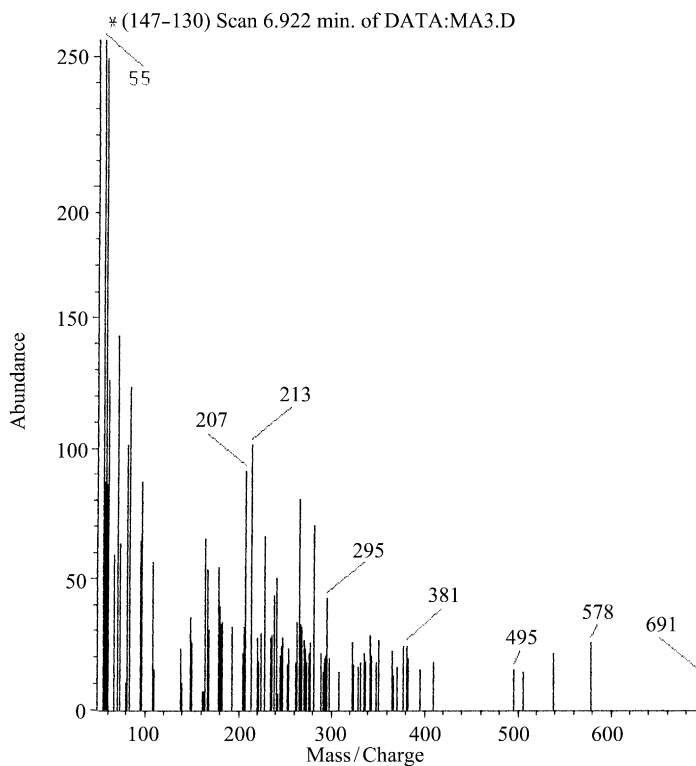


Fig. 10. Mass spectrum of MA3.

about 97.7%. The single mass loss within the temperature range 257.64–450°C is accounted for the loss of CO, CH<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>N(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>CHO, C<sub>6</sub>H<sub>5</sub>NHCOCH<sub>2</sub>CONHC<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>N(C<sub>2</sub>H<sub>5</sub>)COCH<sub>2</sub>CHO and C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> after dissociation of the compound. The DSC curve of MA3 indicates the appearance of three endothermic and one exothermic

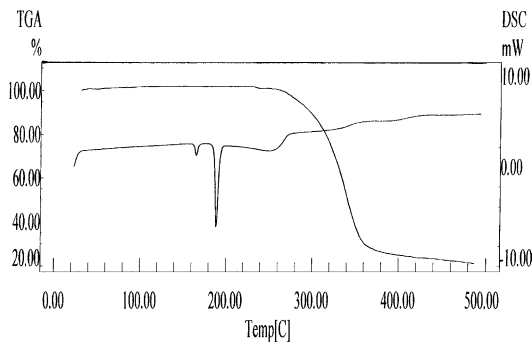
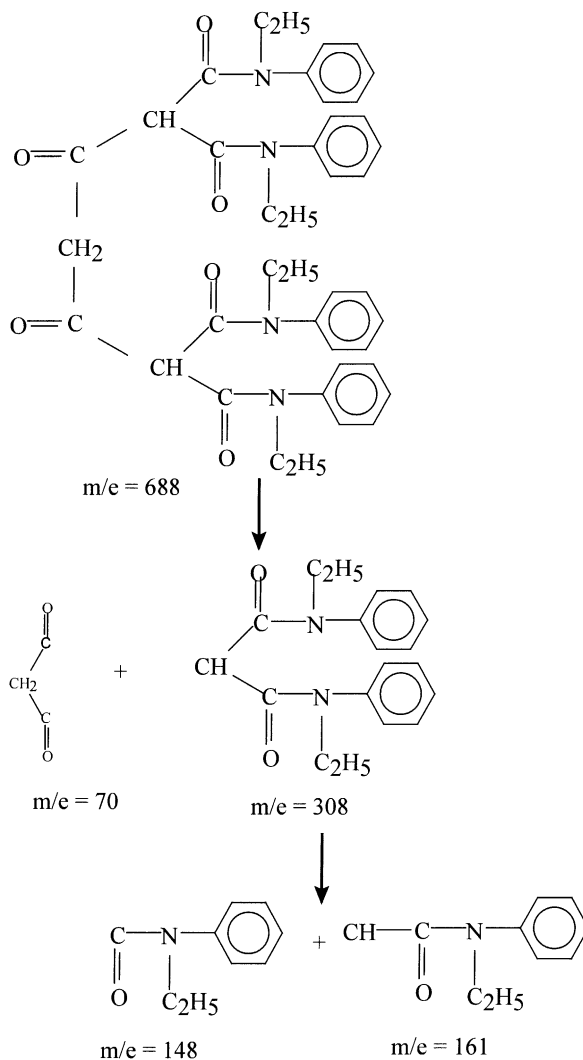
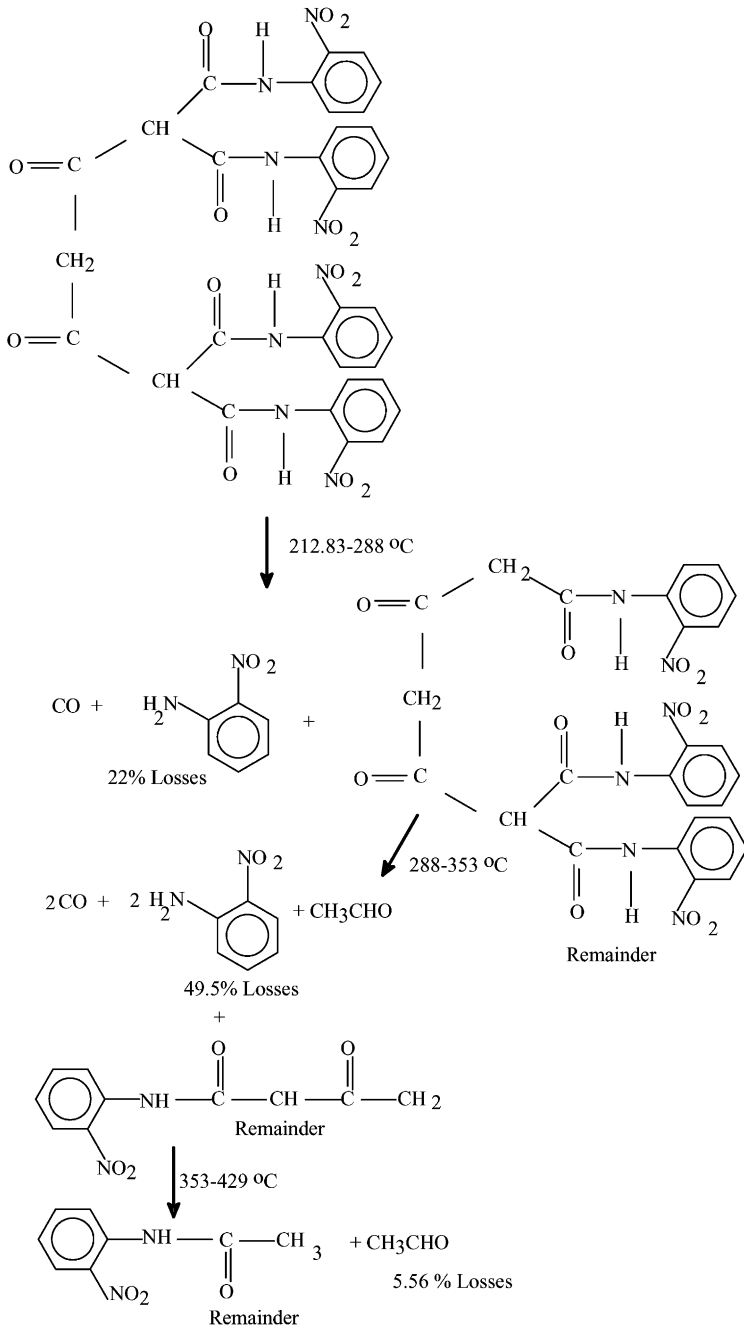


Fig. 11. TGA and DSC of MA4.

peaks. The first sharp endothermic peak at (236°C) is related to the melting of the compound. The second endothermic peak which ranges between 257 and 366°C accounts for the loss of  $2\text{C}_2\text{H}_5$  and  $\text{CH}_2(\text{CO})_2$  fragments. The third exothermic peak (372–420°C) may account for the loss of  $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)\text{COCH}_2\text{CHO}$ ,  $\text{C}_6\text{H}_5\text{NHCOCH}_2\text{CONHC}_6\text{H}_5$  compounds. The fourth endothermic one (420–450°C) may account for the loss of the  $\text{C}_6\text{H}_5\text{NHCH}_3$  compound. The last three peaks are related to the thermal decomposition of the compound. The thermal analysis scheme of decomposition of MA3 dimer is shown in Scheme 3.



Scheme 4.



Scheme 5.

The recorded mass spectra of MA3 is given in Fig. 10. From this spectrum the fragmentation pattern can be represented by the Scheme 4.

Fig. 11 represents the TGA and DSC curves of malonyl *o,o'*-dinitromalonanilide dimer within the temperature range 20–500°C. The TGA curve shows one-step mass loss of about 74.30% which accounts for the loss of 3CO, 2C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)NO<sub>2</sub>, 2CH<sub>3</sub>CHO fragments after the thermal dissociation of the compound. The DSC curve of MA4 indicates the appearance of three endothermic and two exothermic peaks. The first endothermic at 167°C may be related to molecular rearrangement of the compound. The second sharp endothermic one at 194°C is related to the melting of the compound. The third broad endothermic peak (213–288°C) may account for the loss of CO and C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)(NO<sub>2</sub>) fragments. The fourth and fifth exothermic peaks (288–353°C), (353–429°C) may account for the losses of 2CO, 2CH<sub>3</sub>CHO and 2C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)(NO<sub>2</sub>) fragments. The thermal analysis scheme of decomposition of MA4 is shown in Scheme 5.

The recorded mass spectra of MA4 is given in Fig. 12, from this spectrum the fragmentation pattern can be represented Scheme 6.

By comparing the results of the non-isothermal TGA within the decomposition range (DSC results) shown in Table 6 of the propellant samples containing the malonanilides derivatives and the nitrocellulose samples containing the new dimers, it was found that the

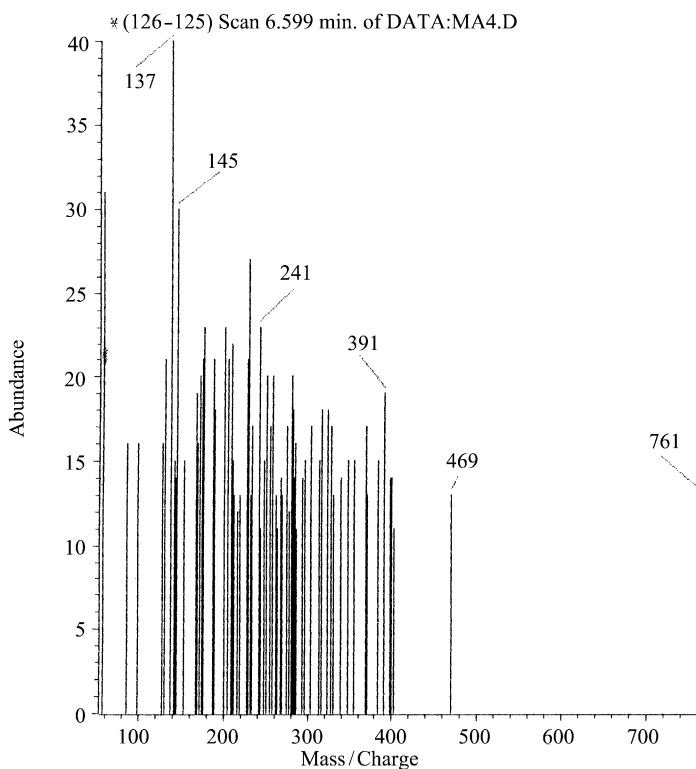
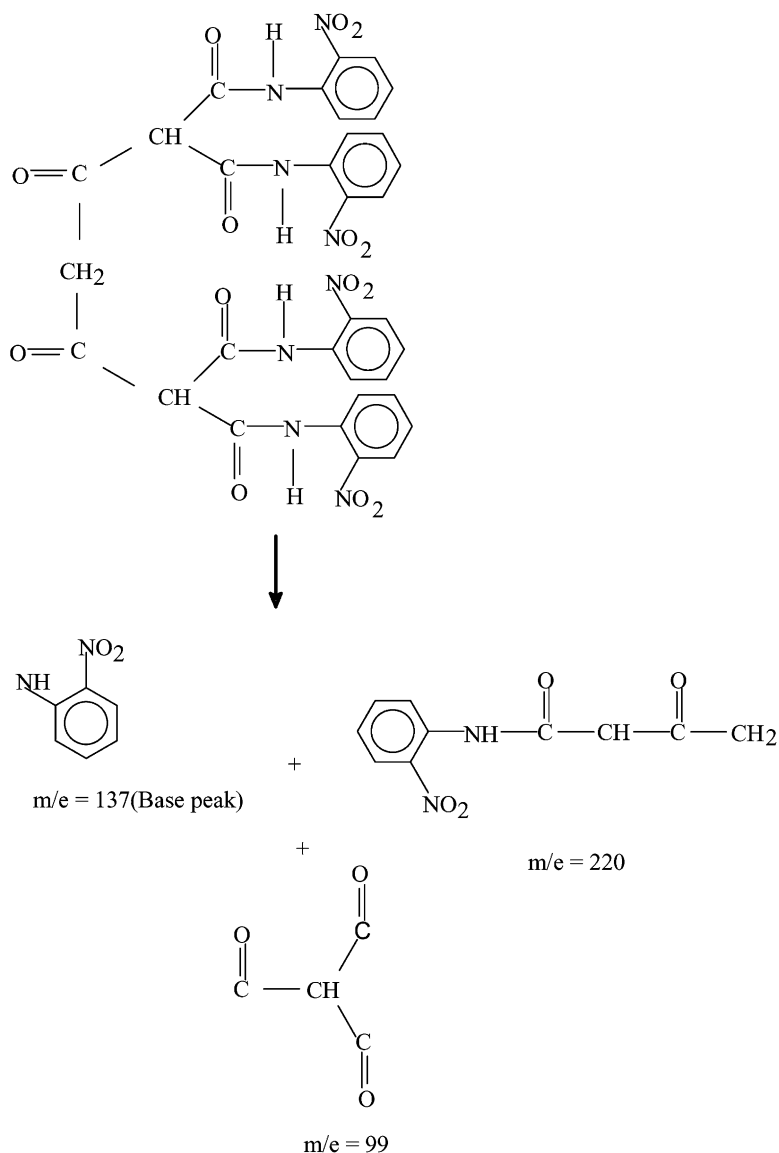


Fig. 12. Mass spectrum of MA4.



Scheme 6.

new MA4 dimer decreases the weight loss by 35.7 in comparison with the *o,o'*-dinitro-malonanilide (M4). In case of adding MA2 dimer the weight loss of the nitrocellulose sample decreased by 37.1%, while the weight loss of the nitrocellulose samples containing the MA3 dimer decreased by 28.71 in comparison with the propellant samples containing the *N,N'*-diethylmalonanilide stabilizer. In general, the new dimers increase the activation energy of decomposition of the nitrocellulose in comparison with malonanilide derivatives.



Table 6

DSC results of propellant samples containing different stabilizers with correlation of TG losses within the decomposition range  $T_i$ – $T_f$

Stabilizers	$T_i$	$T_m$	$T_f$	Weight loss (%)	Activation energy (kJ mol <sup>-1</sup> )
M2	155.6	190.4	210.7	48.3	139.31
M3	160.2	191.7	210.9	65	109.6
M4	151.1	189.8	209.3	45.9	143.43

The MA4 dimer increase the activation energy of nitrocellulose by 12.27 more than the value of propellant sample containing *o,o'*-dinitromalonanilide, The MA2 dimer increases the activation energy by 12.84% and the MA3 dimer increase the value of  $E_a$  by 33.84% more than the value achieved by the corresponding malonanilide derivative (M2&M3).

#### 4. Conclusion

1. The new malonanilide dimers developed in the present work have demonstrated properties as a stabilizers for propellants.
2. Changing the structure of simple malonanilide derivatives into dimer ones increase their stabilizing effect considerably.
3. The malonyl *o,o'*-dinitromalonanilide dimer is considered as the best stabilizer of the different dimers investigated.

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