

## Full Paper

## Stability of Non-isothermally Treated Double-Base Propellants Containing Different Stabilizers in Comparison with Molecular Orbital Calculations

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## Abstract

In this research work some malonanilide derivatives (M1-M5) have been prepared and used as stabilizers for double-base propellants (DBPs). Their stabilization effect has been compared with the effect of *N,N*-diethyldiphenylurea (C1) as a classical stabilizer. Thermal analysis (TA) study under non-isothermal conditions was carried out on propellant samples containing stabilizers. This study gave information about the thermal stability effect of different stabilizers on DBPs, thermal decomposition and some thermodynamic parameters. The non-isothermal (TGA and DSC) results show that the *o*-dinitromalonanilide (M3) has the highest thermal stability effect on the propellant samples. The molecular orbital calculations such as energy gap ( $\Delta E$ ), net charge,  $E_{\text{LUMO}}$ ,  $E_{\text{HOMO}}$ , IP, and  $E_a$  were done and compared with TA experimental data. It was finally concluded that there is no single factor controlling the stabilizing effect of different stabilizers on thermal stability of DBPs. There is a group of factors that play important role in detecting the stabilizing effect of stabilizers on DBPs such as energy gap, charge density on the *o*-position of the benzene ring and the net charge on the benzene ring itself.

**Keywords:** Double-Base Propellants, Malonanilides Stabilizers, Molecular Orbital Calculations, Non-Isothermal (TGA and DTA)

## 1 Introduction

A need exists to improve double-base propellant safe life characteristics through innovations related to the long standing chemical problem of the complex reaction mechanisms known as nitrate ester degradation and its control through chemical stabilizer interaction. During storage of DBPs at elevated temperatures, the stabilizer reacts more and more with the nitrogen oxides ( $\text{NO}_x$ ) released by the nitrate esters (nitrocellulose and nitroglycerin) present in the propellant until it has depleted completely. The need exists for increased propellant performance to support

missions requiring high duty cycles at elevated temperatures and years of operation. The most commonly used double-base stabilizers are diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA), and ethyl centralite (EC) [1–4]

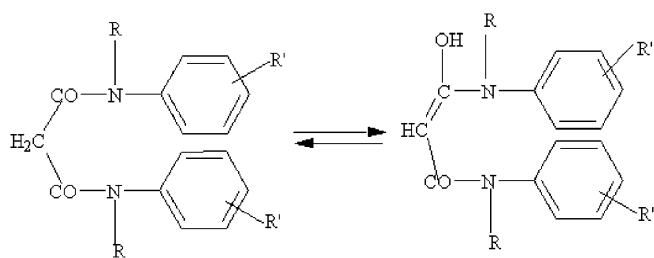
The propellant stabilizers are substances which can react with the products of decomposition of smokeless powders and remove them. They do not prevent decomposition, but they stop the catalytic action of products of decomposition such as  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_2$ , and  $\text{HNO}_3$ . They stabilize the powder by removing the products of decomposition and so the decomposition reaction being uncatalyzed and the powder will have a much longer serviceable life. Stabilizers must possess certain properties [5,6]. A series of researches [7–9] extending over a long period have determined the stabilizing effects of various substances. Many other stabilizers have been examined [10,11].

A number of malonanilide derivatives have found applications as stabilizers for polymers [12,13] and thermal recording materials [14]. In continuation to the previous studies [15–17] the aim of the present work is the search for finding other organic compounds which may show superior properties as stabilizers in comparison with the classical stabilizers under non-isothermal conditions in comparison with molecular orbital calculation results (MOC). Some malonanilides of structures given by Figure 1 are investigated as stabilizers for double base propellants (DBPs).

## 2 Experimental

## 2.1 Materials

The chemicals used in preparation of malonanilides are, ethylmalonate, *N*-ethylaniline, *m*- and *p*-nitroaniline prepared by Merck Schuchart, Germany, of purity 98%, ani-



**M1**, R=H, R'=H

**M2**, R=C<sub>2</sub>H<sub>5</sub>, R'=H

**M3**, R=H, R'=o-NO<sub>2</sub>

**M4**, R=H, R'=m-NO<sub>2</sub>

**M5**, R=H, R'=p-NO<sub>2</sub>

**Figure 1.** Structure formulae of the prepared malonanilides (M1–M5).

line and o-nitroaniline prepared by FIP Germany of purity 98 %.

## 2.2 Instruments

The thermal analyses measurements (TGA and DSC) were made using Shimadzu TGA-50 with platinum cell and Shimadzu DSC-50H with aluminum cell under inert nitrogen atmosphere.

## 2.3 Preparation of Malonanilides

Preparation of M1 itself is well known in literature and it has been prepared by the method of Chattaway [16]. M2 was obtained by heating ethylmalonate with *N*-ethylaniline till boiling for 30 min (yield 73 %), crystallized from acetic acid, m.p. 229.3 °C [16]. Two methods were used to prepare M3, one is old well known in literature [17] and new one [18]. In the new one 500 ml round bottom flask containing 250 ml benzene, 5 g malonic acid, and 13 g o-nitroaniline were added. The mixture was refluxed for 6 h using Dean and Stark apparatus. The solvent was evaporated yielding the M3 product which crystallized from ethanol (m.p. 189 °C). Both M4 and M5 were prepared by mixing 25 ml (1.5 mol) of ethylmalonate with 27.5 g (2 mol) of m-nitroaniline in 250 ml round bottom flask. The mixture was refluxed for 1 h at 200 °C [17].

## 2.4 Preparation of the DBP Samples

Samples of double-base smokeless powders were manufactured by solvent-less process using 3 % centralite (diethylphenylurea) as a reference in sample I and 3 % of malonanilide compounds as stabilizers in samples II–VI. The used percentage of other components is given in Table 1.

Nitroglycerin, dinitrotoluene, dibutylphthalate, stabilizer, and transformer oil were mixed well by gentle stirring for 2 h. The mixture was quantitatively added in small

**Table 1.** The added components in preparation of DBPs.

Composition	Sample %					
	I	II	III	IV	V	VI
Nitrocellulose (12.05 % N)	56	56	56	56	56	56
Nitroglycerin	27	27	27	27	27	27
Dinitrotoluene	9	9	9	9	9	9
Dibutylphthalate	4	4	4	4	4	4
Stabilizer	3	3	3	3	3	3
Transformer Oil	1	1	1	1	1	1

portions to the nitrocellulose continually stirred in a water medium. After the last addition, shaking was continued for 3–4 h to get the complete homogeneity of the mixture. The components were treated according to the different steps used in the production of DBPs. Sample I which was prepared by using 3 % diethyldiphenylurea C1 (Centralite 1) was used as a standard sample to compare the results of the stability tests of the investigated compounds (II–VI).

## 2.5 Molecular Orbital Calculations

The molecular orbital calculations were performed using the empirical AM1 method [19] implemented with the MOPAC6 [20] package.

## 3 Results and Discussion

In this research work some prepared and structurally investigated [18] malonanilides (Figure 1) show superior properties as stabilizers for DBPs in comparison with the classical ones [21–23].

The thermal decomposition of different types of propellants were intensively studied by several authors [21–23], but the effect of stabilizers on thermal decomposition of DBPs using TA techniques is scanty in literature.

### 3.1 Stabilizer Effects on Thermal Behavior of DBPs Under Non-isothermal Conditions

This study involves the use of both TGA and DSC techniques under non-isothermal conditions. The results obtained by both techniques are shown in Tables 2 and 3.

#### 3.1.1 The TGA Under Non-isothermal Conditions

The propellant samples containing different stabilizers are heated under non-isothermal conditions from room temperature to 260 °C using thermogravimetric technique (TGA). The stability of the propellant by addition of stabilizer is indicated by a long time required to reach the maximum rate of thermal decomposition and high temperatures required for starting this decomposition. The data of propellant samples containing classical stabilizer (C1) are represented in Table 2. It appears that the ther-

**Table 2.** Decomposition temperatures of DBPs samples containing different stabilizers from TGA and DTG.

Stabilizers	Temperatures of starting decomposition °C	DTG peak temperatures °C	Rate of maximum weight loss (mg min <sup>-1</sup> )	Time difference between starting decomposition and DTG peak temperatures °C (min)
C1	153.3	203.4	0.29	8.48
M1	153.3	201.6	0.39	8.21
M2	153.0	205.0	0.36	10.00
M3	151.5	223.0	0.53	14.70
M4	155.8	210.0	0.39	13.10
M5	156.0	221.0	0.49	11.00

C1 = *N,N*-diethyldiphenylurea, M1 = Malonanilide, M2 = *N,N*-diethylmalonanilide, M3 = *o*-dinitromalonanilide, M4 = *m*-dinitromalonanilide, M5 = *p*-dinitromalonanilide.

**Table 3.** DSC results of DBP samples containing different stabilizers in comparison with TGA losses within the decomposition temperature range ( $T_f - T_i$ ).

Stabilizers	$T_i$ °C	$T_m$ °C	$T_f$ °C	% Weight loss
C1	162.0	189.1	210.7	80.8
M1	159.0	186.8	213.2	72.5
M2	160.2	191.7	210.9	65
M3	151.1	189.8	209.3	45.9
M4	156.5	188.2	227.3	85
M5	155.6	190.4	210.7	48.3

$T_i$  = temperature of starting decomposition,  $T_m$  = peak temperature and  $T_f$  = temperature of ending decomposition.

mal decomposition of the propellant starts at 153.3 °C. The maximum rate of weight loss is 0.29 mg min<sup>-1</sup> occurring at 203.4 °C (the DTG peak temperature). Also the time difference between the starting of decomposition and reaching the maximum rate of weight loss is 8.4 min. The propellant samples containing new stabilizer M1 start to decompose at 153.3 °C. The maximum rate of weight loss is 0.39 mg min<sup>-1</sup> at temperature 201.6 °C. The time difference between the starting of decomposition and maximum rate of weight loss is 8.21 min. The temperatures of starting decomposition of other propellant samples containing M2, M3, M4, and M5 are 153, 151.5, 155.8, and 156 °C, respectively (Table 2). The temperatures corresponding to maximum rate of weight loss (DTG peak temperature) are 205, 223, 210, and 221 °C for M2–M5, respectively. The time values between the temperature of starting decomposition and the DTG peak temperatures are 10, 14.75, 13.19, and 11 min for M2–M5, respectively. The rates of maximum weight losses are 0.36, 0.53, 0.39, and 0.49 mg min<sup>-1</sup> for M2–M5, respectively. Therefore, from these data it is clear that the new stabilizers (malonanilides) give the DBP samples good thermal stability properties in comparison with the classical stabilizer (C1) and the order of stabilization effect of malonanilides DBP samples is: M3 > M5 > M1, M4, and M2 which nearly have the same stabilizing effects.

### 3.1.2 DSC in Comparison with TGA Under Non-isothermal Conditions

The DSC results in comparison with the TGA are shown in Figure 2 and in Table 3. These results indicate that the propellant samples containing classical stabilizer (C1) de-

composed maximally at peak temperature  $T_m = 189$  °C. On the other hand the propellant samples containing new stabilizers (malonanilides) decompose at  $T_m$  of malonanilide 186.8 °C, of M2  $T_m = 191.7$  °C, of M3  $T_m = 189.2$  °C, of M4  $T_m = 189.2$  °C, and of M5  $T_m = 190.4$  °C. The thermal decomposition of propellant samples containing classical stabilizer occurs in the temperature range between initial temperature ( $T_i = 162$  °C) and final temperature ( $T_f = 210.7$  °C) in comparison with TGA within this range the weight loss % = 80.8. The percentage weight losses of DBPs samples containing new stabilizers (malonanilides) within the decomposition range ( $T_f - T_i$ ) are found to be 45.9% for M3, 48.3% for M5, 65% for M2, 72.5% for M1, and 85% for M4. The results coming from non-isothermal DSC are in good agreement with those coming from non-isothermal TGA. This study also confirms that new stabilizers have better thermal stability effects than the classical one (C1) and M4-isomer. This effect has the following order: M4 < C1 < M1 < M2 < M5 < M3.

### 3.1.3 Calculation of Kinetic Parameters Under Non-isothermal Conditions Using Ozawa Method

Ozawa method [24] was chosen to calculate the kinetic parameters of thermal decomposition of DBP samples containing different stabilizers. Three different heating rates (5, 10, 15 deg min<sup>-1</sup>) were applied and then logarithms of heating rates were plotted against 1/T (Figure 3) corresponding to fixed weight loss (12.84–87.14%), from the slope of the resulted straight lines the activation energy of decomposition could be calculated (Table 4). To calculate the order of the reaction and frequency factor ( $A$ ) of the above process,  $G(x)$  is plotted against reduced time ( $\theta$ ) and the resulted slope is  $A$ .

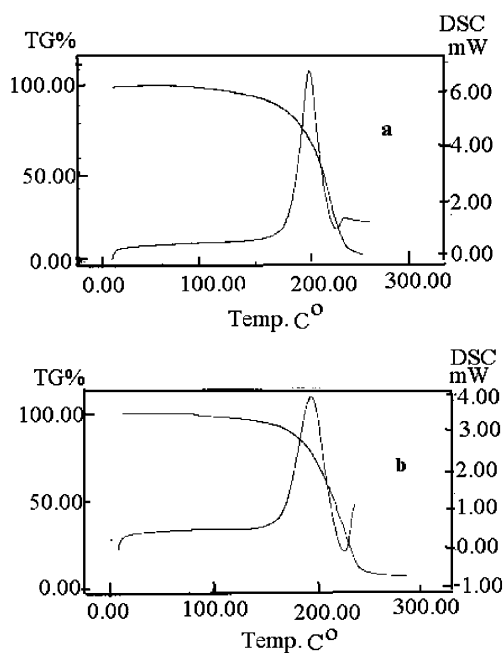
Where,

$$G(X) = 1/n - 1[(1 - C)^{1-n} - 1]$$

$n$  = order of reaction,  $C$  = weight loss percent and

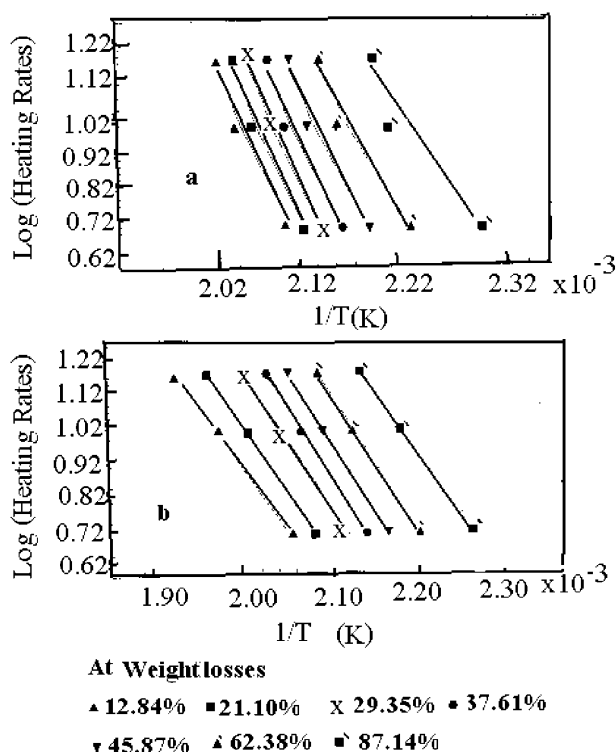
$$\theta = 1/\Phi \int_{T_1}^T \exp(-E_a/RT) dT$$

and  $\Phi$  is the heating rate,  $E_a$  is the activation energy of decomposition.



**Figure 2.** TGA and DSC curves of the propellant samples containing a) C1 and b) M1 as stabilizers.

The plots coming from the above relations for C1 and M1 (as example) are represented in Figure 4 and the calculated kinetic parameters resulting from all plots are shown in Table 4. These results show that the activation



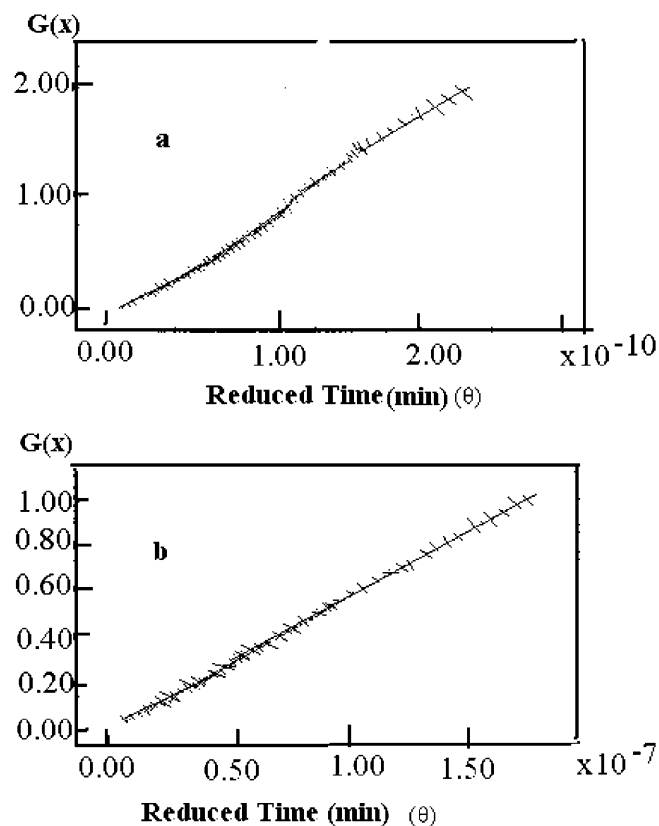
**Figure 3.** Relation between log (heating rates) and  $1/T(K)$  for the propellant samples containing stabilizers: a) C1 and b) M1 within fixed weight loss range (12.84–87.14%).

energy ( $E_a$ ), the frequency factor ( $A$ ), and the order of thermal decomposition ( $n$ ) of propellant samples containing classical stabilizer (C1) are  $93.11 \text{ kJ mol}^{-1}$ ,  $1.027 \times 10^{10} \text{ min}^{-1}$  and 0.8, respectively. The activation energy, the frequency factor, and the order of thermal decomposition of the propellant samples containing M1 are  $70.72 \text{ kJ mol}^{-1}$ ,  $5.64 \times 10^{16} \text{ min}^{-1}$ , and 0.6; of M2 are  $109.6 \text{ kJ mol}^{-1}$ ,  $1.92 \times 10^{11} \text{ min}^{-1}$ , and 0.7; of M3 are  $143.43 \text{ kJ mol}^{-1}$ ,  $1.48 \times 10^{15} \text{ min}^{-1}$  and 1.5; of M4 are  $80.64 \text{ kJ mol}^{-1}$ ,  $5.83 \times 10^7 \text{ min}^{-1}$  and zero; and of M5 are  $139.31 \text{ kJ mol}^{-1}$ ,  $2.25 \times 10^{14} \text{ min}^{-1}$  and 1.2, respectively.

From the above results it is concluded that malonanilides as new stabilizers give the propellant higher thermal stability than the classical one and than M4. The stabilizers generally can be arranged in the order of their thermal stability effects on DBPs in the following order:  $M1 < M4 < C1 < M2 < M5 < M3$ .

### 3.2 Thermal Stability of DBPs Containing Stabilizers and its Correlation with MOCS Parameters

Table 5 lists the HOMO and LUMO energy, energy gap  $\Delta E$ , dipole moment, ml  $\text{NO}_x$  gases,  $E_a$  of decomposition, and the weight loss percent of propellant samples containing stabilizers. These data show that the stabilization effect decreases with the increase of both HOMO and



**Figure 4.** Relation between  $G(x)$  and reduced time ( $\theta$ ) for the propellant samples containing a) C1 and b) M1 as stabilizers within fixed weight losses range (12.88–87.16%).

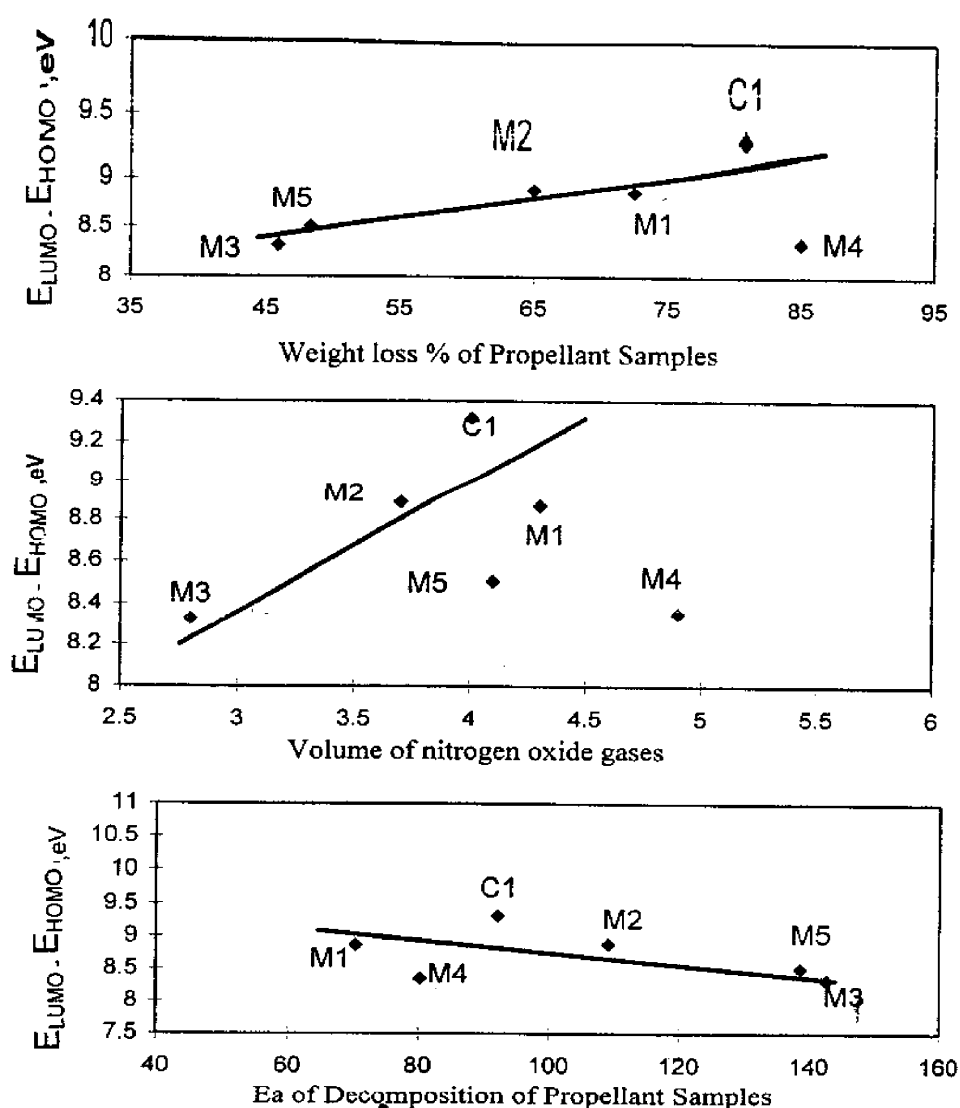
**Table 4.** The kinetic parameters of the thermal decomposition of propellants samples containing different stabilizers from non-isothermal TGA.

Added stabilizer	Activation energy ( $E_a$ , kJ mol <sup>-1</sup> )	Frequency factor (A) min <sup>-1</sup>	Order ( $n$ )
C1	93.11	$1.03 \times 10^{10}$	0.8
M1	70.72	$5.64 \times 10^6$	0.6
M2	109.6	$1.96 \times 10^{11}$	0.7
M3	143.43	$1.48 \times 10^{15}$	1.5
M4	80.64	$5.83 \times 10^7$	0.0
M5	139.31	$2.26 \times 10^{14}$	1.2

LUMO energy values. This means that both *o*- and *p*-nitroisomers (M3 and M5) have the high stabilizing ability for the DBPs.

The correlation between the energy gap  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  and the stability effect of studied stabiliz-

ers expressed as  $E_a$ , their weight loss percent and the volume of NO<sub>x</sub> gases are shown in Figure 5. It is known that  $\Delta E$  is inversely proportional to the reactivity of the molecule [25]. These data also show that, as  $\Delta E$  decreases,  $E_a$  increases while the volume of nitrogen oxide gases liberated decreases and the weight loss of the propellant samples decreases, i.e. stability effect increases. The stabilization effect decreases with the increase in energy gap i.e. with the decrease of the ionization potential (IP) and consequently the direction of easy ionization of molecules. The correlation between the energy gap  $\Delta E$  and  $E_a$  of decomposition is better than that with the volume of NO<sub>x</sub> gases evolved. The electron donating ability of such compounds increases with increasing  $\Delta E$  in the following order, M1 > M4 > C1 > M2 > M5 > M3. Consequently, the order of stabilization effect of added stabilizers can be represented in the following manner: M3 > M5 > M2 >



**Figure 5.** The relation between the energy gap ( $\Delta E = \text{HOMO-LUMO}$ ) and the stabilization effect of different stabilizers: C1 = *N,N*-diethylidiphenyl urea, M1 = malonanilde, M2 = *N,N*-diethylmalonanilde, M3 = *o*-dinitromalonanilde, M4 = *m*-dinitromalonanilde, M5 = *p*-dinitromalonanilde.

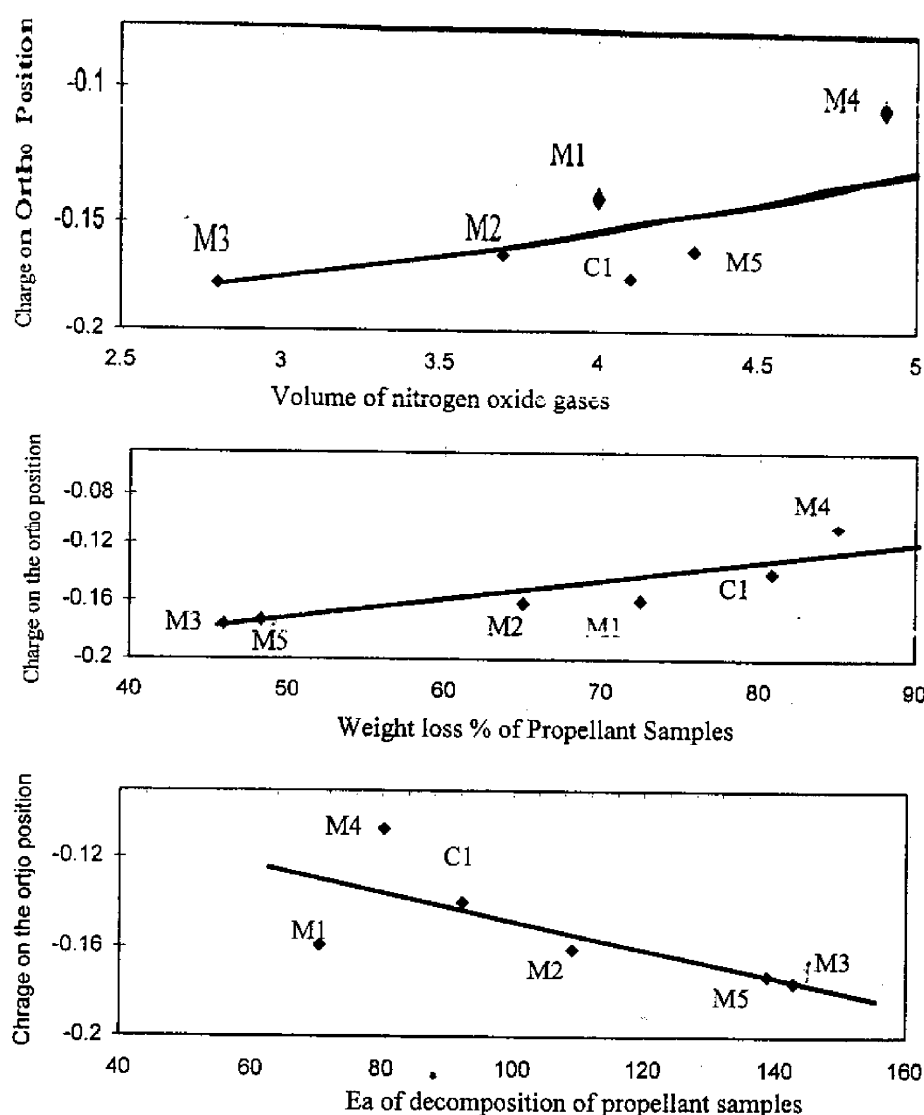
**Table 5.** The calculated values for  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap,  $\Delta E$ , ionization potential, IP, and dipole moment for stabilizers.

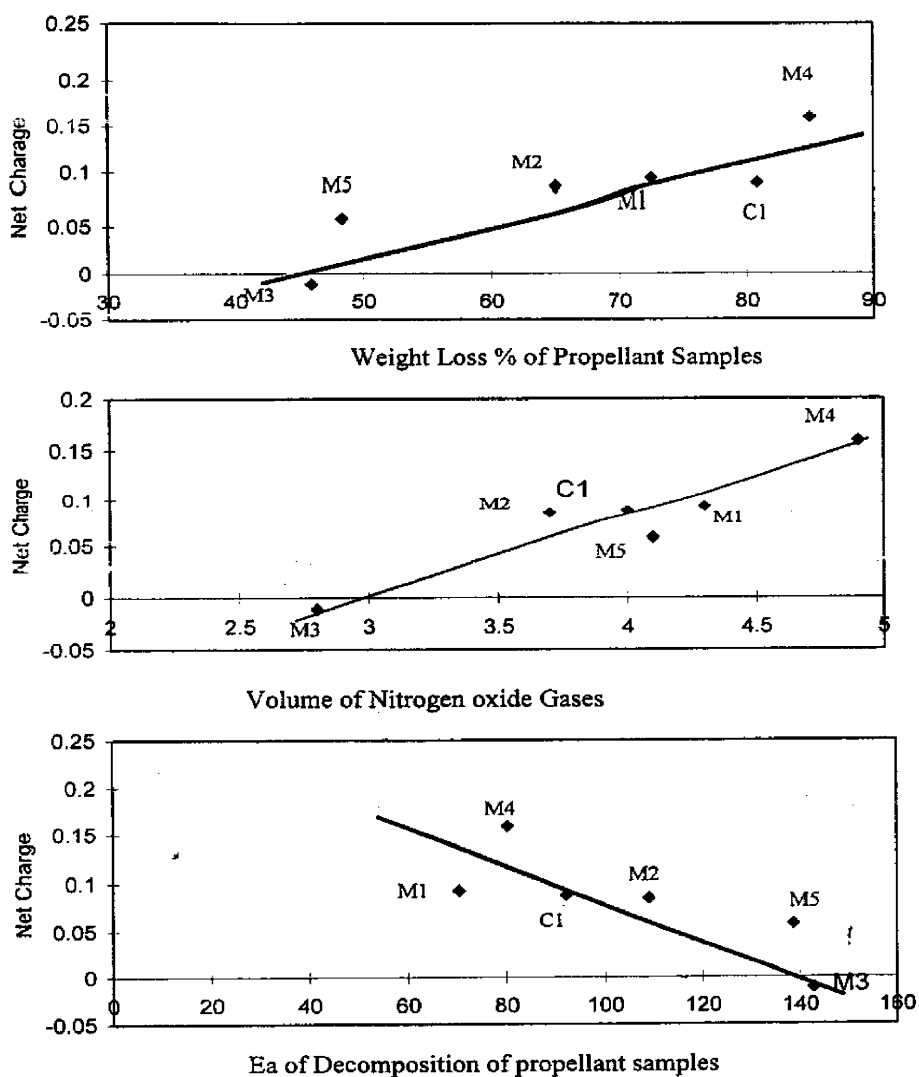
Stabilizers	$E_{\text{HOMO}}$ , eV	$E_{\text{LUMO}}$ , eV	$\Delta E$ , eV	I.P., eV	Dipole moment, D	ml $\text{NO}_x$ gases	Weight loss%	$E_a$ ( $\text{kJ mol}^{-1}$ ) of decomposition
C1	-9.003	0.3141	9.317	-9.003	2.297	4.0	80.8	93.11
M1	-8.869	-0.00146	8.869	-8.869	1.800	4.3	72.5	70.72
M2	-8.724	0.1631	8.888	-8.724	2.284	3.7	65.0	109.6
M3	-9.587	-1.2670	8.327	-9.587	1.458	2.8	45.9	143.43
M4	-9.671	-1.3197	8.352	-9.671	5.072	4.9	85.0	80.64
M5	-9.903	-1.3953	8.508	-9.903	7.298	4.1	48.3	139.31

$C1 > M4 > M1$ . This means that M3 of small  $\Delta E$  has high reactivity to react with  $\text{NO}^+$  ions liberated and accordingly has the high ability to stabilize DBPs.

Figure 6 displays the correlation between the net charge on o- or p-position and that concentrated charge on the benzene ring with stabilization effect. From these

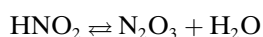
results it is clear that o-dinitro derivative shows the highest value of negative charge ( $-0.011$ ) while m-dinitro derivative shows the highest positive value of charge ( $0.159$ ). The correlation between the net charge and parameters measured for the stabilization effect gives good correlation. Different mechanisms were suggested to ex-


**Figure 6.** The relation between the net charge on ortho position of the stabilizers and the stabilization effect of different stabilizers: C1 = *N,N*-diethyldiphenyl urea, M1 = malonanilide, M2 = *N,N*-diethylmalonanilide, M3 = *o*-dinitromalonanilide, M4 = *m*-dinitromalonanilide, M5 = *p*-dinitromalonanilide.



**Figure 7.** The relation between the energy gap ( $\Delta E = \text{HOMO-LOMO}$ ) and the stabilization effect of different stabilizers: C1 = *N,N*-diethyldiphenyl urea, M1 = malonanilide, M2 = *N,N*-diethylmalonanilide, M3 = *o*-dinitromalonanilide, M4 = *m*-dinitromalonanilide, M5 = *p*-dinitromalonanilide.

plain the role of different stabilizers in stabilizing the propellants [26–29]. It was assumed that the first step is the reaction of  $\text{NO}^+$  produced from nitrocellulose decomposition with the nitrogen atom of the stabilizer to form *N*-nitroso derivative as given,



Where  $\text{y} = \text{NO}_3^-$  and  $\text{~~~~}$  = the stabilizer moiety.

The second step is the rearrangement of the formed *N*-nitroso to  $\text{C}_6\text{-NO}$  or  $\text{C}_6\text{-NO}_2$  of the benzene ring [30–32]. Therefore the charge on *N*-atoms and factors increasing it has an important role in fixation of nitrogen oxides on the stabilizer.

Figure 7 represents the charge distribution e.g. of C1 and M1. The high negative charge is concentrated on oxygen atom of CO group and on the nitrogen at connected to the ring (center of attack). The magnitude of charge density on nitrogen atom is found to be high in case of M3, while the low density is in case of C1 as a classical stabilizer. Consequently, the first step in the suggested mechanism will be faster in case of new stabilizers than the classical one and *o*-dinitromalonanilide will be fastest one. The order of charge density on the nitrogen atom for such compound is given as,  $\text{M3} > \text{M1} > \text{M4} > \text{M5} > \text{M2} > \text{C1}$ .

The charge on the ortho or para position as the active site depends on the presence of the substituent and its position. The charge decreases in the following order,  $\text{M3} > \text{M5} > \text{M2} > \text{M1} > \text{C1} > \text{M4}$ , which is the trend of their stabilization effect (Table 5).

## 4 Conclusion

The use of non-isothermal TGA and DSC study for DBPs containing both classical and newly prepared stabilizers can evaluate and differentiate between their stabilization effects. From the obtained results it is clear that the stability of the propellant by addition of stabilizer is indicated by long time required to reach the maximum rate of thermal decomposition and high temperatures required for starting this decomposition. From Ozawa non-isothermal calculation, it is concluded that malonanilides as new stabilizers give the propellant higher thermal stability than the classical one and than M4. The stabilizers generally can be arranged in the order of increasing their thermal stability effects on DBPs in the following order: M1 < M4 < C1 < M2 < M5 < M3.

It is more convenient to use theoretical MOCS parameters to confirm such differentiation. The correlation between the energy gap  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  and the stability effect of studied stabilizers is expressed as  $E_a$  of decomposition of propellant samples, their weight loss percent and the volume of  $\text{NO}_x$  gases. These data also show that as  $\Delta E$  decreases, the activation energy of the propellant sample increases while the volume of nitrogen oxide gases liberated decreases and the weight loss of the propellant samples decreases i.e. stability effect increases. This means that M3 of small  $\Delta E$  has high reactivity to react with  $\text{NO}^+$  ions liberate and accordingly has the high ability to stabilize DBPs.

## References

- [1] J. McGovern, *Improved Stability of Double Base Propellants*, Navy SBIR 2009.2 – Topic N092-109.
- [2] K. J. Mitchell, *Effects of Desert Thermal Environment on Army Propulsion Systems*, U.S. Army Missile Command, Redstone Arsenal, AL, May 2009.
- [3] A. Fun, R. Dudley, *Treatment of Accelerated Aging Data using First Order Reaction Equations*, Picatinny Arsenal, Picatinny, NJ, March 2009.
- [4] J. Drummond, J. Lawhon, A. Gonzales, H. Shimm, Spheroidal Propellant Stabilizer Studies, St. Marks Powder, General Dynamics Company, CPIA, *JANNAF 30th Propellant Development and Characterization Subcommittee Meeting*, March 18–21, 2002, Colorado Springs, CO, United States, CPIA-Publ-708-Vol-1.
- [5] T. Lindblom, Reactions in Stabilizer and Between Stabilizer and Nitrocellulose in Propellants, *Propellants, Explos., Pyrotech.* **2002**, 27 (4), 197.
- [6] J.-J. Jutier, Y. Harrison, S. Premont, R. E. Prud'homme, A Nonisothermal Fourier Transform Infrared Degradation Study of Nitrocelluloses Derived from Wood and Cotton, *J. Appl. Polym. Sci.* **2003**, 33 (4) 1359.
- [7] J. M. Bellerby, M. H. Sammour, Stabilizer Reactions in Cast Double Base Rocket Propellants. Part II: Formation and Subsequent Reactions of N-Nitroso Derivatives of Para-Nitro-N-Methylaniline and 2-Nitrodiphenylamine in Mixed-Stabilizer Propellants Aged at 80 °C and 90 °C, *Propellants, Explos., Pyrotech.* **2004**, 16 (6), 273.
- [8] M. Marquayrol, Study of Different Stabilizers, *Membr. Poudres* **1928**, 23, 158.
- [9] A. Venter, D. R. Ifa, R. G. Cooks, S. K. Poehlein, A. Chin, D. Ellison, A Desorption Electrospray Ionization Mass Spectrometry Study of Aging Products of Diphenylamine Stabilizer in Double-Base Propellants, *Propellants, Explos., Pyrotech.* **2006**, 31 (6) 472.
- [10] R. A. Pesce-Rodriguez, P. E. Marsh, Nitric Oxide Depth-Profiles of Aged Double-Based Gun Propellants, **2002**, <http://handle.dtic.mil/100.2/ADA407984>.
- [11] S. N. Asthana, B. Y. Deshpande, H. Singh, Evaluation of Various Stabilizers for Stability and Increased Life of CMDB, *Propellants, Explos., Pyrotech.* **2004**, 14 (4), 170.
- [12] M. Coquillat, Ageing of Polybutadiene Based Propellants: Kinetic Modeling of Oxidation. *PhD thesis Mécanique et Matériaux, ENSAM, ENAM0021* **2007**, 186.
- [13] Sumitomo Chemical Company Ltd, *Manufacture of Industrial Chemicals, Plastics, Pharmaceuticals, Aluminum, Synthetic Rubber, Dyestuffs and Fine Chemicals, Pesticides, Electronic Products*. Report Overview Manufacturing, May 13, 2009.
- [14] S. C. Kim, D. Klemperer, K. C. Frisch, H. L. Frisch, Polyurethane Interpenetrating Polymer Networks. 4. Volume Resistivity Behavior of Polyurethane-Poly(Methyl Methacrylate) Interpenetrating Polymer Networks, *Macromolecules* **1977**, 10 (6), 1191.
- [15] J. T. Moyer, Y. Yogo, M. J. Zaiser, H. Tsukahara, Spawning Behavior and Social Organization of the Flounder *Crossorhombus Kobensis* (Bothidae) at Miyake-Jima, *Jpn. Jap. J. Ichthyol.* **1985**, 32(3), 363.
- [16] F. D. Chattaway and J. M. D. Olmsted, LXIX. – The Action of Aromatic Amines on Ethyl Malonate, *J. Chem. Soc., Trans.* **1910**, 97, 938.
- [17] W. A. Jacobs, M. Heidelberger, The Ferrous Sulfate and Ammonia Method for the Reduction of Nitro- to Aminocompound, *J. Am. Chem. Soc.* **1917**, 39, 1435.
- [18] M. A. M. Hassan, Malonanilides as Stabilizers for Double-Base Propellants, *Ph.D. Thesis, Cairo University, Egypt* **1998**.
- [19] M. J. S. Dewar, W. Thiel, Ground States of Molecules, 38. The MNDO Method. Approximations and Parameters. *J. Am. Chem. Soc.* **1977**, 99, 4899.
- [20] Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47405 USA, QCPE 62, **1964**.
- [21] M. A. Zayed, A. A. W. Soliman, M. A. Hassan, Evaluation of Malonanilides as New Stabilizers for Double-Base Propellants, *J. Hazard. Mater.* **2000**, B 73, 237.
- [22] P. V. R. Verneker, K. Kishore, B. K. Chaturvedi, M. Ramathan, Some Observations on Sublimation and Decomposition of Ammonium Perchlorate, *Propellants, Explos., Pyrotech.* **1981**, 6 (6), 158.
- [23] T. Shimizu, J. Kimura, *J. Jpn. Explos. Soc.* **1996**, 57 (1), 28.
- [24] T. Ozawa, A New Method of Analyzing Thermogravimetric Data, *Bull. Chem. Soc. Jpn* **1965**, 38, 1881.
- [25] R. G. Pearson, Recent Advances in the Concept of Hard and Soft Acids and Bases, *J. Chem. Educ.* **1987**, 64, 561.
- [26] J. Tranchant, Internal Mechanism of the Chemical Evaluation of Nitrocellulose Propellants; Hypothesis and Consequences, *6th Jan Hansson Symposium on Chemical Problems Connected with the Stability of Explosives*, Kungälv, Sweden, June 13–17, **1982**.
- [27] A. Alm, Studies on Reactions between Nitrogen Oxides and Diphenylamine Compounds, *1st Jan Hansson Symposium on Chemical Problems Connected with the Stability of Explosives*, Stockholm, Sweden, May 22–23, **1967**.
- [28] M. Dreyfus, *Stabilité chimique des propergols homogènes et leur surveillance*, Report No. 2441, **1988**, Etablissement Technique de Bourges. – Defence Research Information Centre, Translation-8413, Procurement Executive, Ministry of Defence, UK.



- [29] B. A. Lur'e, B. S. Svetlov, The Kinetics and Mechanism of the Thermal Decomposition of Nitrocellulose, *LS-TRANS-1894*, **1980**, Vol. I (12), 5–14. Atomic Weapons Establishment, Aldermaston, UK.
- [30] B. C. Challis, M. R. Osborne, The Chemistry of Nitroso Compounds. Part VI: Direct and Indirect Reaction of N-Nitrosodiphenylamine, *J. Chem. Soc. Perkin Trans.* **1973** 2, 1526.
- [31] L. D. Biggs, D. H. L. Williams, The Kinetics and Mechanism of the Fischer-Hepp Rearrangement and Denitrosation, Part V: The Mechanism of Denitrosation, *J. Chem. Soc., Perkin Trans.* **1975**, 2, 107.
- [32] S. S. Johal, The Kinetics and Mechanism of Denitrosation of Nitrosamine in Ethanol, *J. Chem. Soc., Perkin Trans.* **1980**, 2, 165.