

Thermal behavior, specific heat capacity and adiabatic time-to-explosion of G(FOX-7)

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Abstract

[H₂N=C(NH₂)₂]⁺(FOX-7)⁻-G(FOX-7) was prepared by mixing FOX-7 and guanidinium chloride solution in potassium hydroxide solution. Its thermal decomposition was studied under the non-isothermal conditions with DSC and TG/DTG methods. The apparent activation energy (*E*) and pre-exponential constant (*A*) of the two exothermic decomposition stages were obtained by Kissinger's method and Ozawa's method, respectively. The critical temperature of thermal explosion (*T_b*) was obtained as 201.72 °C. The specific heat capacity of G(FOX-7) was determined with Micro-DSC method and theoretical calculation method and the standard molar specific heat capacity is 282.025 J mol⁻¹ K⁻¹ at 298.15 K. Adiabatic time-to-explosion of G(FOX-7) was also calculated to be a certain value between 13.95 and 15.66 s.

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1. Introduction

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high energy material with high thermal stability and low sensitivity to impact and friction. When synthesized firstly in 1998 [1], FOX-7 received much attention immediately. Many researches have been carried out on the synthesis, mechanism, molecular structure, thermal behavior, explosive performance and applications of FOX-7 [2–11]. FOX-7 is a nitro-enamine belonging to the group of compounds known as “push–pull” alkenes [12], and possesses a highly polarized carbon–carbon double bond with positive and negative charges being stabilized by the two amino groups and the two nitro groups respectively. FOX-7 exists in manifold tautomers and resonances, and presents different struc-

tural forms within the pH range of 1–13 (Scheme 1) [3,4,6]. So, FOX-7 can react with some nucleophiles and strong alkalis to synthesize new energetic compounds. Through synthesis of [H₂N=C(NH₂)₂]⁺(FOX-7)⁻-G(FOX-7), we expect to increase nitrogen content in the molecule, produce more clean gas in thermal decomposition and combustion process, and use it as a potential gas generator and additive in propellant.

In this paper, we studied the thermal behavior of G(FOX-7) under the non-isothermal condition with DSC and TG/DTG methods, determined its specific heat capacity with Micro-DSC method and theoretical calculation method, and calculated its adiabatic time-to-explosion.

2. Experimental

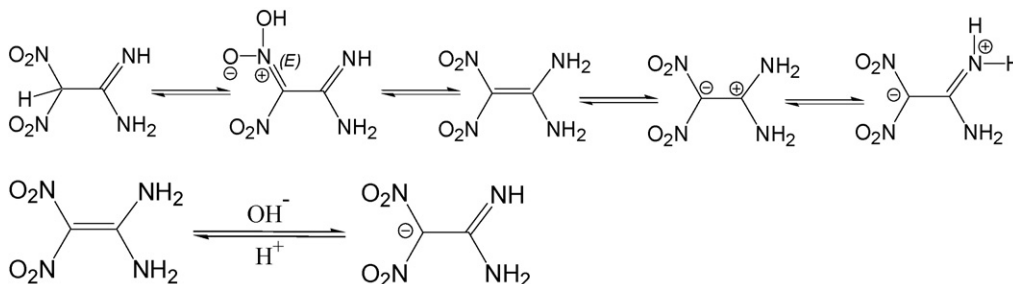
2.1. Sample

G(FOX-7) used in this research was prepared as follows [5]: FOX-7 (0.01 mol, 1.48 g) was suspended in 15 ml of water and to it a solution of KOH (1.12 g in 5 ml water) was added drop wise. After complete dissolution, guanidinium chloride solution

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Scheme 1.

(0.96 g in 5 ml water) was also added drop wise. After reacting at room temperature for 30 min, the resulting mixture was cooled to 0 °C. Faint yellow crystals of G(FOX-7) were formed, which was filtered, washed with ice water and dried under vacuum, yielding 1.41 g (68%). Anal. calcd. for $C_3H_9N_7O_4$ (%): C 17.39, H 4.39, N 47.33; found (%): C 17.46, H 4.38, N 46.33. The characteristic peaks of IR (KBr) are: 3431, 3448, 1659, 1570, 1477, 1372, 1343, 1246, 1208, 1114 cm^{-1} .

Single crystal suitable for X-ray diffraction measurement was obtained by slow evaporation of the above filtrate at 0 °C for three days. Crystallographic data for G(FOX-7): orthorhombic, space group $P-bca$, $a = 1.0428(3)$ nm, $b = 0.73099(18)$ nm, $c = 2.2253(5)$ nm, $F(000) = 864$, $V = 1.6963(7)$ nm³, $Z = 8$ and $D_c = 1.622$ g cm⁻³, which have been deposited in the Cambridge Data Center, CCDC number: 658013. The molecular structure is shown in Fig. 1.

2.2. Experimental equipments and conditions

The DSC and TG-DTG experiments for G(FOX-7) were performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 ml min⁻¹. The amount of used sample was about 1 mg. The heating rates used were 2.5, 5, 10 and 15 °C min⁻¹ from ambient temperature to 500 °C.

The specific heat capacity of G(FOX-7) was performed using a Micro-DSCIII apparatus (SETARAM, France) and the amount

of used sample was 442.37 mg. The heating rate used was 0.15 °C min⁻¹ from 10 to 80 °C, in which the precisions of temperature and heat flow were 10⁻⁴ °C and 0.2 μW, respectively. The principle for measuring of the continuous specific heat capacity is shown as:

$$C_p = \frac{A_s - A_b}{m_s \times \beta} \quad (1)$$

where C_p is the specific heat capacity, A_s and A_b are the heat flows of the sample and blank, m_s is the amount of the sample, β is the heating rate.

2.3. Theoretical calculation of specific heat capacity

According to the crystal structure, a crystal unit was selected as the initial structure, while HF/6-311++G** method in Gaussian 03 package [13] was used to optimize the structure of G(FOX-7) and compute its frequencies at different temperatures. We can get a series of thermodynamic data of G(FOX-7) based on the statistic thermodynamic theory. At the same time, vibration analysis showed that the optimized structure is in accord with the minimum points on the potential energy planes, which means no virtual frequencies, proving that the optimized structure is stable and our calculation results is reliable. All the convergent precisions are the system default values, and all the calculations were carried out on the personal *Lenovo* computer.

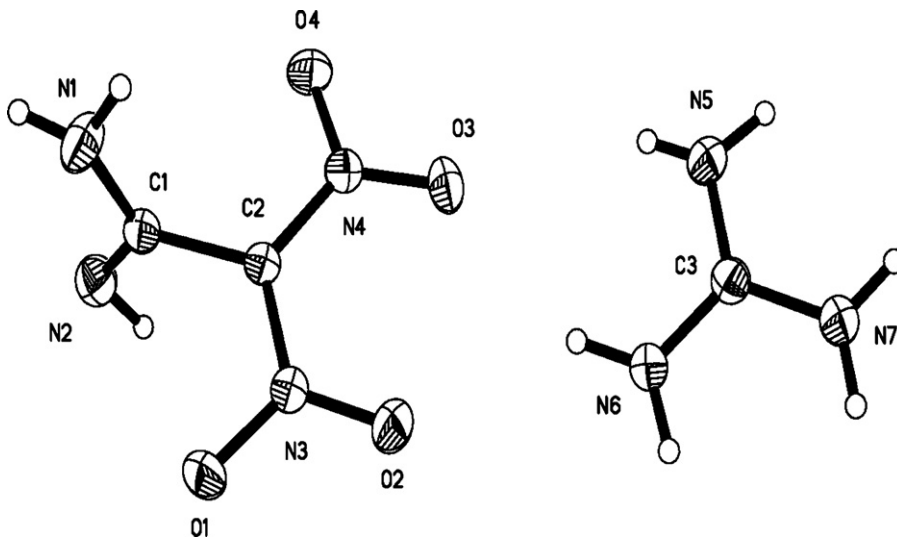


Fig. 1. Molecular structure of G(FOX-7).

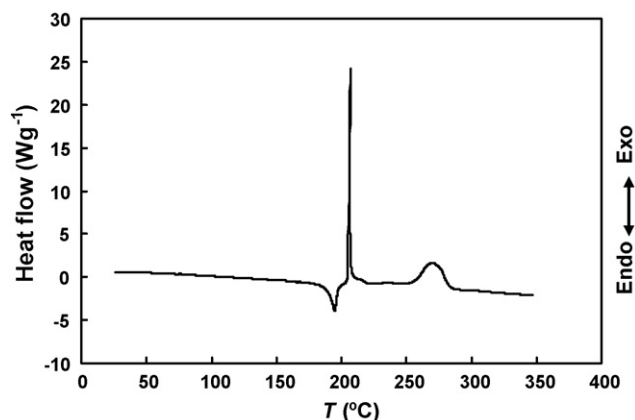


Fig. 2. DSC curve of G(FOX-7) at a heating rate of $5^{\circ}\text{C min}^{-1}$.

3. Results and discussion

3.1. Thermal behavior

Typical DSC and TG/DTG curves of G(FOX-7) are shown in Figs. 2 and 3.

From the DSC curve, we can see that the thermal behavior of G(FOX-7) can be divided into three stages. The first stage is a melting process of G(FOX-7), and the extrapolated onset temperature (T_e), peak temperature (T_m) and melting enthalpy (ΔH_m) obtained at the heating rate of $5^{\circ}\text{C min}^{-1}$ are 180.38°C , 187.02°C and 41.16 kJ mol^{-1} , respectively. The other two stages are the exothermic decomposition processes. The first exothermic decomposition process occurs at $195.20\text{--}211.85^{\circ}\text{C}$ with a mass loss of about 20.7%, and the second exothermic decomposition process occurs at $263.82\text{--}271.13^{\circ}\text{C}$ with a mass loss of about 33.6%. But, there is still a very unobvious exothermic decomposition process between the two obvious exothermic decomposition processes with a mass loss of about 10.9%, which can be testified by TG/DTG curves.

In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the two obvious exothermic decomposition reaction for G(FOX-7), a multiple heating method (Kissinger's method [14] and Ozawa's

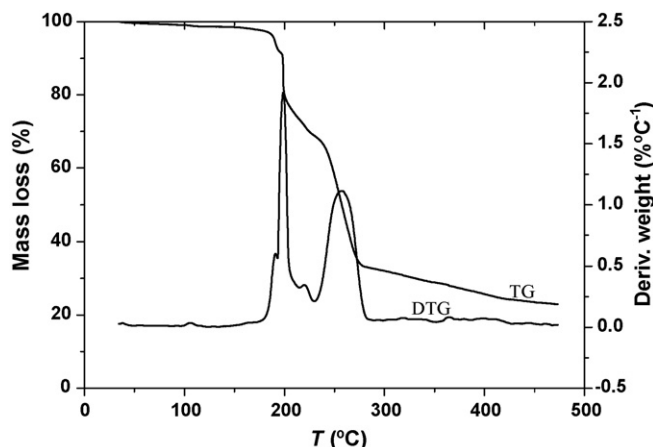


Fig. 3. TG/DTG curves of G(FOX-7) at a heating rate of $5^{\circ}\text{C min}^{-1}$.

method [15]) was employed. The Kissinger and Ozawa equations are as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_k} - \frac{E_k}{R} \frac{1}{T_p} \quad (2)$$

$$\log\beta + \frac{0.4567E_O}{RT_p} = C \quad (3)$$

where β is the linear heating rate, T_p is the peak temperature, A is the pre-exponential constant, R is the gas constant, E is the apparent activation energy and C is a constant.

The original values (the beginning temperature (T_0), extrapolated onset temperature (T_e), peak temperature (T_p) and enthalpy of the exothermic decomposition reaction (ΔH_d)) of the two exothermic decomposition reactions at various heating rate were listed in Tables 1 and 2. The above-mentioned values (E and A) determined by Kissinger's method and Ozawa's method and the liner correlation coefficients (r) were also listed in Tables 1 and 2, respectively.

The values (T_{00} , T_{e0} and T_{p0}) of T_0 , T_e and T_p corresponding to $\beta \rightarrow 0$ obtained in the two exothermic decomposition stages by Eq. (4) were all shown in Tables 1 and 2.

$$T_{(0,e\text{ or }p)i} = T_{(00,e0\text{ or }p0)} + n\beta_i + m\beta_i^2, \quad i = 1\text{--}4 \quad (4)$$

where n and m are coefficients.

From the results, we can see that the apparent activation energy obtained by Kissinger's method is in good accord with that obtained by Ozawa's method, moreover, the liner correlation coefficients are all very close to 1. So, the result is credible.

The critical temperature of thermal explosion (T_b) obtained by Eq. (5) taken from Ref. [16] is 201.72°C .

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O RT_{e0}}}{2R} \quad (5)$$

where E_O is the value of the apparent activation energy obtained by Ozawa's method.

The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) of the first exothermic decomposition stage corresponding to $T = T_{p0}$ and $E = E_k$ obtained by Eqs. (6)–(8) taken from Ref. [17] are $98.64\text{ J mol}^{-1}\text{ K}^{-1}$, $183.38\text{ kJ mol}^{-1}$ and $137.44\text{ kJ mol}^{-1}$, respectively.

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (6)$$

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (7)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (8)$$

where k_B is the Boltzman constant and h is the Plank constant.

Table 1

The values of T_0 , T_e , T_p , ΔH_d , T_{00} , T_{e0} , T_{p0} , E_k , $\log A$, r_k , E_O and r_O for G(FOX-7) determined from the DSC curves at various heating rate (β) in the first exothermic decomposition stage^a

β ($^{\circ}\text{C min}^{-1}$)	T_0 ($^{\circ}\text{C}$)	T_e ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	ΔH_d (kJ mol^{-1})	T_{00} ($^{\circ}\text{C}$)	T_{e0} ($^{\circ}\text{C}$)	T_{p0} ($^{\circ}\text{C}$)	E_k (kJ mol^{-1})	$\log A$ (s^{-1})	r_k	E_O (kJ mol^{-1})	r_O
2.5	191.16	195.09	195.81									
5.0	195.20	198.71	198.80									
10.0	201.71	205.54	205.79	74.15	186.96	191.41	192.59	183.38	18.14	0.9663	181.90	0.9690
15.0	207.01	212.02	212.75									

^a Subscript k is data obtained by Kissinger's method, subscript O is data obtained by Ozawa's method.

Table 2

The values of T_0 , T_e , T_p , ΔH_d , T_{00} , T_{e0} , T_{p0} , E_k , $\log A$, r_k , E_O and r_O for G(FOX-7) determined from the DSC curves at various heating rate (β) in the second exothermic decomposition stage^a

β ($^{\circ}\text{C min}^{-1}$)	T_0 ($^{\circ}\text{C}$)	T_e ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	ΔH_d (kJ mol^{-1})	T_{00} ($^{\circ}\text{C}$)	T_{e0} ($^{\circ}\text{C}$)	T_{p0} ($^{\circ}\text{C}$)	E_k (kJ mol^{-1})	$\log A$ (s^{-1})	r_k	E_O (kJ mol^{-1})	r_O
2.5	226.49	232.99	247.40									
5.0	236.82	242.66	257.14									
10.0	250.27	256.35	270.60	105.28	213.81	221.44	235.65	135.31	10.99	0.9975	137.13	0.9978
15.0	254.24	262.52	276.03									

^a Subscript k is data obtained by Kissinger's method, subscript O is data obtained by Ozawa's method.

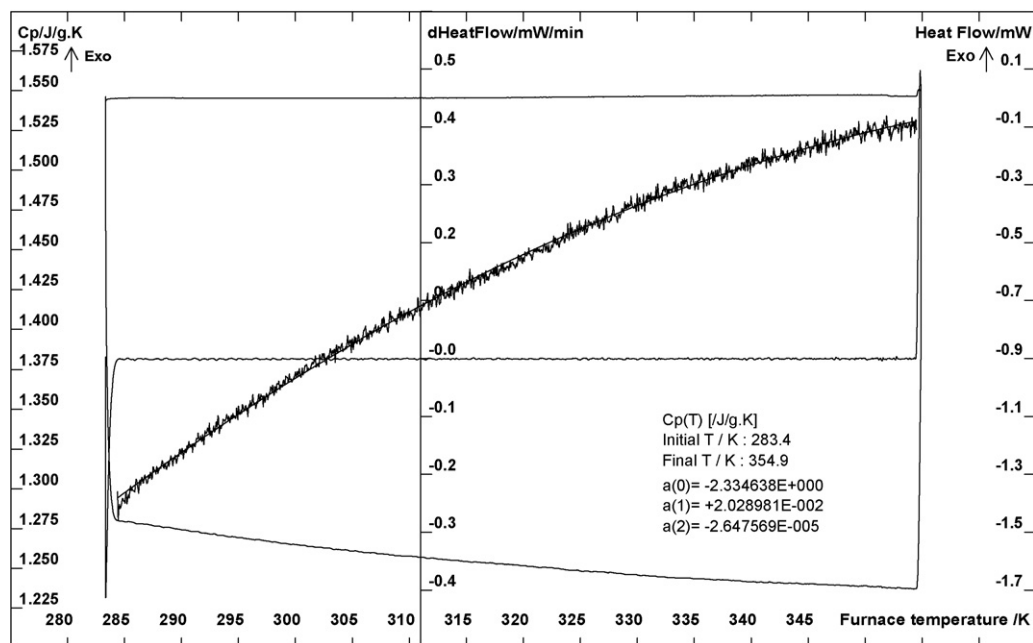


Fig. 4. Determination results of the continuous specific heat capacity of G(FOX-7).

3.2. Specific heat capacity

Fig. 4 shows the determination results of G(FOX-7), using continuous specific heat capacity mode of Micro-DSCIII apparatus. In determined temperature range, specific heat capacity of G(FOX-7) presents a good quadratic relationship with temperature. Specific heat capacity equation is shown as:

$$C_p(\text{J g}^{-1} \text{K}^{-1}) = -2.3346 + 2.0290 \times 10^{-2}T - 2.6476 \times 10^{-5}T^2 \quad (283 \text{ K} < T < 353 \text{ K}) \quad (9)$$

The standard molar specific heat capacity of G(FOX-7) is $282.025 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K . Although only 70 K range was taken in the determining process, the specific heat capacity equation obtained is a stable and continuous equation, which can provide a reference and some help for the wide temperature applications.

According to the result of frequency calculation, there is no imaginary frequency. It shows that the theoretical calculation is reliable. Table 3 shows the results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviations at different temperatures. We can see that the calculated results are all less than experimental results, and the relative deviations are comparatively great, from 18.36% to 21.49%. The reason for the result is that only gas-phase molecule was used in theoretical calculation process, which is clearly different to actual solid phase molecule.

3.3. Adiabatic time-to-explosion

Energetic materials need a time from the beginning thermal decomposition to thermal explosion in adiabatic condition. We called the time as the adiabatic time-to-explosion [17–19].

Ordinarily, we use heating rate (dT/dt) and critical heating rate $(dT/dt)_{T_b}$ in thermal decomposition process to evaluate the thermostability of energetic materials. However, we can calculate the adiabatic time-to-explosion (t) by the following Eqs. (10)–(12) [17,18] when we have obtained a series of experimental data. Thereby, it is very easy and intuitionistic to evaluate the thermostability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_p \frac{dT}{dt} = QA \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (10)$$

$$f(\alpha) = (1 - \alpha)^n \quad (11)$$

Table 3

Results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviation at different temperatures

Temperature (K)	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)		RD (%)
	Theoretical calculation value	Experimental value	
283.0	217.7	266.6	18.3
288.0	220.1	272.0	19.1
293.0	222.5	277.1	19.7
298.0	224.9	281.9	20.2
303.0	227.4	286.4	20.6
308.0	229.8	290.7	20.9
313.0	232.2	294.7	21.2
318.0	234.6	298.4	21.4
323.0	237.0	301.8	21.5
328.0	239.5	305.0	21.5
333.0	241.9	307.9	21.4
338.0	244.3	310.5	21.3
343.0	246.7	312.8	21.1
348.0	249.1	314.9	20.9
353.0	251.5	316.7	20.6

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (12)$$

where C_p is the specific heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), t is the adiabatic time-to-explosion (s), Q is the exothermic values (J mol^{-1}), A is pre-exponential factor (s^{-1}), E is the apparent activation energy of the first exothermic stage (J mol^{-1}), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), $f(\alpha)$ is the most probable kinetic model function, n is the rate order and α is the fraction of conversion.

According to the above determining results of G(FOX-7), we use:

$$C_p = a + bT + cT^2 \quad (13)$$

where a , b and c are coefficients.

The combination of Eqs. (10)–(13) gives the following equation:

$$\begin{aligned} t &= \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{QAf(\alpha)} dT \\ &= \frac{1}{QA} \int_{T_0}^T \frac{(a + bT + cT^2) \exp(E/RT)}{(1 - \alpha)^n} dT \\ &= \frac{1}{QA \{1 - (1/Q)[a(T_b - T_{00}) + (b/2)(T_b^2 - T_{00}^2) + (c/3)(T_b^3 - T_{00}^3)]\}^n} \\ &\quad \int_{T_0}^T (a + bT + cT^2) \exp(E/RT) dT \end{aligned} \quad (14)$$

The limit of the temperature integration in Eq. (14) is from T_{00} to T_b .

Presuming that the rate order (n) of the thermal explosion of G(FOX-7) equals 0, 1 and 2, we can directly get $t_0 = 13.95$ s, $t_1 = 14.78$ s and $t_2 = 15.66$ s from Eq. (14), according to the above experimental results and neglecting the effect of the melting and other changes. As a rule, the rate order (n) of energetic materials ranges from 0 to 2, so the adiabatic time-to-explosion of G(FOX-7) is a certain value between 13.95 and 15.66 s, a short time, and it can be proved credible according to the change of DSC curve in the first exothermic decomposition stage.

4. Conclusion

- (1) The thermal behavior of G(FOX-7) was studied. The values of the apparent activation energy of the two exothermic decomposition stages are 183.35 and 135.31 kJ mol^{-1} obtained by Kissinger's method, and 182.53 and 136.87 kJ mol^{-1} by Ozawa's method, respectively. The values of pre-exponential constant (A) of the two exothermic decomposition stages are $10^{19.91}$ and $10^{12.77} \text{ s}^{-1}$. The critical temperature of thermal explosion (T_b) is 201.72 °C.
- (2) The specific heat capacity of G(FOX-7) was determined. Specific heat capacity equation is $C_p (\text{J g}^{-1} \text{K}^{-1}) = -2.3346 + 2.0290 \times 10^{-2}T - 2.6476 \times 10^{-5}T^2$ ($283 \text{ K} < T < 353 \text{ K}$). The standard molar specific heat capacity is 282.025 $\text{J mol}^{-1} \text{K}^{-1}$ at 298.15 K.

- (3) The adiabatic time-to-explosion of G(FOX-7) was calculated to be a certain value between 13.95 and 15.66 s.

Acknowledgments

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