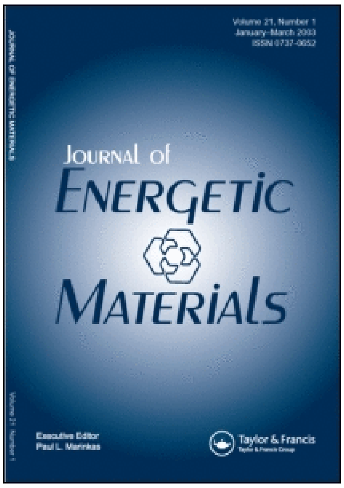

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

A new ignition criterion based upon a critical thermal energy density

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To cite this Article Taihua, Zhang and Taohua, Bian(2001) 'A new ignition criterion based upon a critical thermal energy density', Journal of Energetic Materials, 19: 4, 305 — 337

To link to this Article: DOI: 10.1080/07370650108216131

URL: http://dx.doi.org/10.1080/07370650108216131

A NEW IGNITION CRITERION BASED UPON A CRITICAL THERMAL ENERGY DENSITY

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ABSTRACT

It has long been known that various ignition criteria of energetic materials have been limited in applicability to small regions. In order to explore the physical nature of ignition, we calculated how much thermal energy per unit mass of energetic materials was absorbed under different external stimuli. Hence, data of several typical sensitivity tests were analyzed by order of magnitude estimation. Then a new concept on critical thermal energy density was formulated. Meanwhile, the chemical nature of ignition was probed into by chemical kinetics.

Journal of Energetic Materials Vol. 19, 305-337 (2001)
Published in 2001 by Dowden, Brodman & Devine, Inc.

Finally, it was considered that perhaps the critical thermal energy density was an important characteristic parameter for energetic material ignition.

INTRODUCTION

For several decades, many sensitivity tests have solved some issues on safety and reliability, but application ranges are strictly limited. In general, sensitivities are usually expressed by quantities of external stimuli, for example, the environmental temperature of one-dimensional time to explosion and explosion temperature tests [1-2], critical drop-height of impact and friction tests, critical thickness of gap tests, pressure and pulse width of shock ignition tests, energy and heat flux density of laser ignition tests [3]. In fact, these ways are unable to reflect how much energy energetic materials absorb from external stimuli. Since energetic materials indicate different response to varied external stimuli, sensitivities are not characteristic parameters of ignition. They only show a kind of rough correspondence to external stimuli, therefore various sensitivities are short of correlations [4].

It was found by numerous tests that sensitivities of energetic materials not only depend upon the nature of the external stimuli, but also depend upon their physical properties (heat capacity and thermal conductivity), chemical properties (chemical structure and activation energy), charge conditions and so on. All of the above properties strongly influence energetic materials in absorbing energy and inducing chemical reaction. We analyze several typical sensitivity data from a new viewpoint of absorbing thermal energy. The main purpose of the analysis is to seek characteristic parameters that affect ignition, to probe ignition mechanisms, and to identify inherent relationships.

ORDER OF MAGNITUDE ESTIMATES

Thermal, mechanical, shock, and laser stimuli are able to induce ignition in energetic materials. Despite these different stimulus forms, the ignition mechanisms may come down to thermal action. In fact, the concept of a thermal ignition mechanism is well accepted. In this paper, we pay attention to how much thermal energy energetic materials absorb from external stimuli when they are ignited. This thermal energy is defined as the thermal energy absorbed per unit mass of energetic material. We give some typical examples (as follows) to estimate the order of magnitude of thermal energy densities for common energetic materials, and explain some experimental phenomena.

One-Dimensional Time to Explosive (ODTX)

In the LLNL (Lawrence Livermore National Laboratory) ODTX test [1], 2.2g samples (12.7mm diameter sphere) are placed between two preheated anvil faces (76.2mm diameter × 50.8mm high) in which the temperature is T. The unit is sealed to confine the detonation product gases. The anvils are heated electrically; the temperature is controlled by thermocouple feedback. Times to explosion, t, are measured as a function of temperature. The heat capacities, c, of TNT (trinitrotoluene), RDX (1,3,5- trinitro-1,3,5-triazacyclohexane), Comp. B (Composition B), are assumed as constants, here given in c= 1.51 kJ/(kg·K), 1.13 kJ/(kg·K), 1.25 kJ/(kg·K) [1], respectively. All initial temperature of energetic materials is assumed as T_0=293K. The thermal energy density is written as

$$e = c(T - T_0) = c\Delta T \, .$$

The experimental data and results are listed in TABLE 1.

TABLE 1

One-dimensional time to explosion

TNT			RDX			Comp. B		
t (s)	ΔT (K)	e (kJ/g)	t (s)	ΔT (K)	e (kJ/g)	t (s)	ΔT (K)	e (kJ/g)
6920	190	0.28	7590	159	0.18	7940	153	0.19
2290	210	0.32	1740	161	0.18	3980	157	0.20
832	230	0.35	759	163	0.18	3970	158	0.20
302	243	0.37	525	171	0.19	3020	160	0.20
115	263	0.40	363	173	0.20	1200	161	0.20
39.8	277	0.42	302	179	0.20	380	170	0.21
15.8	290	0.44	191	181	0.20	251	172	0.21
			120	182	0.21	110	177	0.22
			87.1	186	0.21	50.1	189	0.24
			45.7	198	0.22	25.1	198	0.25
			28.8	207	0.23	16.1	207	0.26
			14.5	214	0.24	12.0	220	0.27

Explosion Temperature

In Ref [2], a 20mg sample of explosive, loosely loaded in a No.8 blasting cap, is immersed for a short period in a Wood's metal bath. The temperature determined is that which produces explosion, ignition or decomposition of the sample in a few seconds, and the behavior of the samples is indicated by "Explodes" or "Ignites" or "Decomposes" placed beside the value. The explosion temperature is the lowest temperature for explosion, ignition, decomposition of energetic materials heated under the certain conditions. The thermal energy density is written as

$$e = c(T - T_0) = c\Delta T .$$

The experimental data are listed in TABLE 2.

TABLE 2

Explosion temperature

TNT			RDX			Comp. B		
t (s)	ΔT (K)	e (kJ/g)	t (s)	ΔT (K)	e (kJ/g)	t (s)	ΔT (K)	e (kJ/g)
10	445	0.67	15	215	0.24	10	235	0.29
5	455	0.69	10	220	0.25	5	258	0.32
1	500	0.76	5	240	0.27	1	348	0.44
0.1	550	0.83	1	296	0.33	0.1	506	0.63
			0.1	385	0.44			

Thermal Ignition at High Pressure

In Ref [5], a fixed quantity of electrical energy is discharged into a no. 479 platinum heater of R=1Ω resistance and $d_{Pt}=6.35\times10^{-3}$cm diameter. The heater is located in the center of a 0.75g sample housed in a fixture that permits pressurized loading of the specimen. The test is performed by discharging a fixed quantity of electrical energy into the sample. The static pressure load is varied according to a 25-shot Bruceton "up and down" procedure. The explosive's 50% probability of an ignition response is obtained with respect to a specific combination of pressure and energy. This test is repeated at several energy levels providing data that are used to determine the relative effectiveness of additives to desensitize RDX/TNT (60/40) against hotspot ignition. A measurement of the energy delivered to the heater was obtained for each shot in the Bruceton series.

The thermal energy delivered by the platinum heater is

$$Q = UIt = \frac{U^2}{R}t$$

and the heating time is

$$t = Q\frac{R}{U^2} \approx 4.0 \times 10^{-6} s \ .$$

The resistivity of platinum is $\rho=10.5\times10^{-8}\Omega m$ [6], and the length of platinum is

$$L = S \cdot R/\rho = \pi d_{Pt}^2/4 \cdot R/\rho = 3.0 \times 10^{-2} m \ .$$

The mass, density and diameter of sample are $m_B=7.5\times10^{-4}$kg, $\rho_B=1690$kg/m^3, $D=1.27\times10^{-2}$m, respectively. So the thickness of sample is

$$h = \frac{m_B}{\rho \frac{\pi D^2}{4}} = 3.5 \times 10^{-3} m .$$

The thermal conductivity and heating time of Comp. B are K=0.26W/(m·K) and t=4.0×10^{-6}s, and the heated thickness of the sample is

$$\delta = \sqrt{\frac{Kt}{\rho_B c_B}} = 7.0 \times 10^{-7} m .$$

Therefore, the masses of sample $(\delta < h)$ and platinum heated respectively are

$$m_B = \rho_B \cdot \frac{\pi}{4}[(d_{Pt} + 2\delta)^2 - d_{Pt}^2] \cdot L$$

$$m_{Pt} = \rho_{Pt} \cdot \frac{\pi d_{Pt}^2}{4} \cdot L .$$

It is assumed that there is the same temperature between the platinum and heated Comp. B. The density and heat capacity of platinum are ρ_{Pt}=21.44g/cm^3, c_{Pt}=0.138kJ/(kg·K) [6], then the thermal energy absorbed in Comp. B is

$$Q_B = Q[\frac{c_B m_B}{c_B m_B + c_{Pt} m_{Pt}}] = 0.03Q\,.$$

The thermal energy density thereby is written as

$$e = \frac{Q_B}{m_B}\,.$$

The experimental data and results are listed in TABLE 3.

TABLE 3

Thermal ignition with high pressure

Capacitor Charge (V)	90	110	130	150
Thermal Energy (J)	0.0288	0.0517	0.0690	0.0950
Threshold Pressure (MPa)	126.6	96.6	83.0	71.0
Heating Time (µs)	4.0	4.0	4.0	4.0
Thermal energy density (kJ/g)	0.13	0.23	0.31	0.42

Friction Ignition

The experiment was designed to pressurize an explosive sample by the high pressure activator [7]. The arrangement, designed to test explosive sliding against a steel surface, is shown in cross section in FIGURE 1(a). A short cylinder of explosive was placed within a steel confinement cylinder. A polyethylene buffer plug was butted against each face of the explosive sample, and then the transfer and velocity pistons were slide into place as shown. The purpose of the polyethylene buffer plugs was to prevent spurious ignition caused by steel on steel friction in the region adjacent to the explosive sample. The radius and length of sample are R=6.35mm, L=12.7mm, respectively. The experiments have a relatively long duration of about one millisecond, a maximum velocity of about 80m/s. The experimental results, FIGURE 1 (b) and (c), show that the ignition threshold depends on both the pressure and velocity.

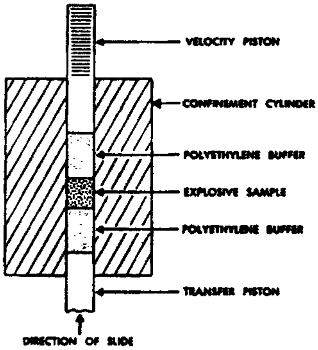


FIGURE 1(a)

Test arrangement for explosive sliding on steel [7]

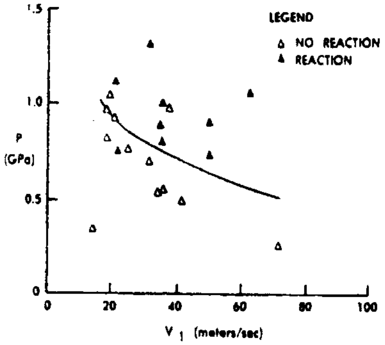


FIGURE 1(b)

Data for TNT sliding against steel [7]

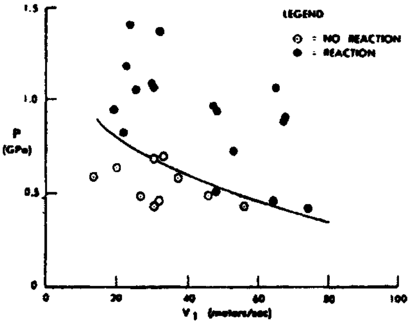


FIGURE 1(c)

Data for Comp. B sliding against steel [7]

Open symbols indicate no reaction, and closed symbols indicated reaction. The solid curve represents the boundary between reaction and non-reaction.

We analyze again the experimental results as follows. Since the pressure is far more than the yield strength of TNT and Comp. B, the work done by frictional forces acting on a sliding explosive is

$$W = f \cdot vt/2 = 2\pi RL \cdot P/2 \cdot \mu \cdot vt/2$$

where P denotes the maximum pressure, v the maximum velocity of the piston, t the duration of pressure, μ the friction coefficient. The average friction force and sliding velocity were derived from the half of maximum pressure and velocity of the piston. Within pressurization time t, the heated thickness in energetic materials and the steel cylinder are

$$\delta = \sqrt{\mathrm{K}t/\rho c}$$

$$\delta_{Fe} = \sqrt{\mathrm{K}_{Fe}t/\rho_{Fe}c_{Fe}}\ .$$

The ratio of thermal energy absorbed by energetic materials is

$$\begin{aligned}\alpha &= cm\Delta T/[cm\Delta T + c_{Fe}m_{Fe}\Delta T] \\ &= cA\delta\rho/[cA\delta\rho + cA\delta_{Fe}\rho_{Fe}] \\ &= 1/[1+\sqrt{c_{Fe}\rho_{Fe}\mathrm{K}_{Fe}/c\rho\mathrm{K}}]\end{aligned}$$

The thermal energy density is written as

$$e = \alpha W/m = \alpha W/2\pi RL \cdot \delta \cdot \rho = \frac{1}{4} \cdot \alpha \cdot \mu \cdot \frac{1}{\rho} \cdot \frac{1}{\sqrt{K/\rho c}} \cdot Pv \cdot \sqrt{t}\ .$$

We assumed: (A) ρ、μ、c、K of the steel cylinder and energetic materials are constants, respectively; (B) For most of the tests, the pressurization duration, t, of all the experiments were about the same, so $\sqrt{t}$ is regarded as a constant, namely t=1.0ms; (C) The dynamic friction coefficient between nylon and steel is 0.3~0.5, and 0.05~0.1 if the lubricant is added [8]. Because the melting points of TNT and Comp. B are lower, the surface of sample would have melted during it was pressurized, and the friction velocity in the tests is faster than the handbook [8]. So, the friction coefficient is obtained as μ=0.06. Under the certain conditions,

$$\beta = \frac{1}{4} \cdot \alpha \cdot \mu \cdot \frac{1}{\rho} \cdot \frac{1}{\sqrt{K/\rho c}} \cdot \sqrt{t} = constant\ .$$

The thermal energy density is given by the following relation

$$e = \beta \cdot Pv \qquad (1)$$

The experimental data and results are indicated in TABLE 4.

In FIGURE 1 (b) and (c), the curves of Ref. [7] defined by

$Z = v^2 \exp(P/P_0) = constant$ separate ignitions from non-ignitions. Moreover, the analysis supports the idea that ignition thresholds depend on both pressure and velocity and appeared to properly separate ignitions and non-ignition. In comparison with of the Ref [7], the model is in good agreement with the experimental data. In sum, the model gives a concrete criterion, and its physics significance is clearer than Ref. [7].

TABLE 4

Friction ignition

	α	β ((m^2·s)/kg)	P (GPa)	V (m/s)	E (kJ/g)
TNT	0.06	5.0×10^{-5}	0.9	20	0.9
Comp. B	0.05	4.0×10^{-5}	0.8	22	0.7

Shearing Ignition

In Ref [7], for explosive on explosive shear, the arrangement is shown in FIGURE 2(a). In this case, the explosive sample was clamped within steel sleeves and a plug was sheared out of its center. End plates kept the sleeves from moving during the experiment. The arrangement could be placed in the high pressure activator. The radius and length of sample are R=9.525mm, L=12.7mm, respectively. The experiments have a relatively long duration of about one millisecond, a maximum shearing velocity of about 80m/s. The experimental results are shown in FIGURE 2(b). The conclusion indicated: (A) both pressure and shear velocity have a strong effect on ignition; (B) the relation $v^2 \exp(P/P_0) = constant$ appeared to properly separate ignitions and no ignitions in the tests; (C) the results of sliding and shearing tests are similar.

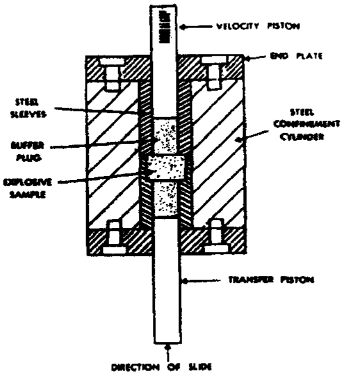


FIGURE 2(a)

Test arrangement for explosive shearing [7]

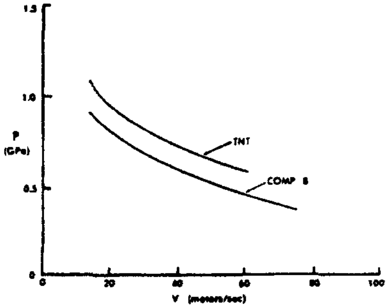


FIGURE 2(b)

Summary curves for shearing tests [7]

We analyze again the experimental results as follows. The dynamic friction coefficients of nylon on nylon are 0.1~0.2 [8] if some lubricants exit between them. The pillow is polyethylene material, and the sample surface, considering the lower melting points of TNT and Comp. B, might have melted, hence the friction coefficient of polyethylene vs. TNT and Comp. B are obtained as $\mu=0.1$. Since the maximum shear stress F is between μPA(0.1PA) and PA, we obtain F=0.5PA, where average shear stress and average velocity are taken to be half of their max. values. The shear work is

$$W = 2 \cdot F/2 \cdot vt/2 = \pi R^2 \cdot P/2 \cdot vt/2 \, .$$

The shear field thickness δ is 0.1mm~10mm, so we get δ=1mm. The mass of shear field is

$$m = A\delta\rho = 2\pi R \cdot L \cdot \delta \cdot \rho \, .$$

During the sliding process, the absorption depths in the sample and the pillow of polyethylene respectively are

$$\delta = \sqrt{\mathrm{K}t/\rho c}$$
$$\delta_p = \sqrt{\mathrm{K}_p t/\rho_p c_p} \, .$$

The absorption coefficient of the sample is

$$\begin{aligned}\alpha &= cm\Delta T/[cm\Delta T + c_P m_P \Delta T] \\ &= cA\delta\rho/[cA\delta\rho + c_P A\delta_P \rho_P] \\ &= 1/[1 + \sqrt{c_P \rho_P \mathrm{K}_P / c\rho\mathrm{K}}]\end{aligned}$$

The thermal energy density is

$$e = \alpha W/m = \frac{1}{8} \cdot \alpha \cdot \frac{R}{L} \cdot \frac{1}{\delta} \cdot \frac{1}{\rho} \cdot Pv \cdot t\,.$$

We assumed: (1) ρ、μ、c、**K** are constants; (2) Since the sliding times in the tests were approximately consistent, the times may be regarded as a constant, namely t=1.0ms. Therefore, $\beta = \frac{1}{8} \cdot \alpha \cdot \frac{R}{L} \cdot \frac{1}{\delta} \cdot \frac{1}{\rho} \cdot t$ is a constant under the experimental conditions. The thermal energy density is given by the following relation

$$e = \beta \cdot Pv \qquad (2)$$

The experimental data and results are indicated in TABLE 5.

TABLE 5

Shearing ignition

Energetic Materials	α	$\beta(m^2 \cdot s)/kg$	P(GPa)	v(m/s)	e(kJ/g)
TNT	0.50	2.9×10^{-5}	0.7	40	0.8
Comp. B	0.46	2.6×10^{-5}	0.6	40	0.6

The above relation may distinctly explain the three experimental results of Ref [7]: (A) both pressure and shear velocity have a strong effect on ignition; (B) the relation (2) appeared to properly separate ignitions and non-ignitions. In comparison with the relation $v^2 \exp(P/P_0) = constant$, the relation $e = \beta \cdot Pv$ indicates more valid; and (C) the two forms of relations (1) and (2) are the same, and their values of β, P, v come near, hence the two types of tests exited approximate results.

Laser Igniting Pyrotechnic Mixture (PM)

A 300W CO_2-laser (λ=10.6μm) was used to heat a pyrotechnic mixture (PM) of MG and $NaNO_3$ at various power levers and pulse widths [3]. The Gaussian intensity distribution was transformed to a rectangular transverse intensity by a beam integrator. This was imaged on the sample through a lens, and the irradiated area was measured by making an imprint in plexiglass. The area was about 3.0mm^2, so the laser beam radius was 0.94mm. The specification related to the PM sample is shown in TABLE 6(a).

TABLE 6(a)

Specification of the PM sample

Composition $58\%Mg+42\%NaNO_3$	Sample size Φ10mm×2mm
Grain size	Density 1650kg/m^3(85%)
Mg, spec MIL-P-140C7B(95%<45μm)	Heat capacity 1.0kJ/(kg·K)
$NaNO_3$, sieved (<75μm)	Thermal conductivity 4.4W/(m·K)
Compacting pressure 150-160MPa	

In the delay time, the absorption depth in the sample is given as

$$\delta = \sqrt{Kt/\rho c}\ .$$

The heated field is displayed in FIGURE 3(a), and its volume is

$$V = \frac{\pi}{6}\cdot\delta\cdot\{3[(R+\delta)^2 + R^2] + \delta^2\}\ .$$

Thermal energy density is written as

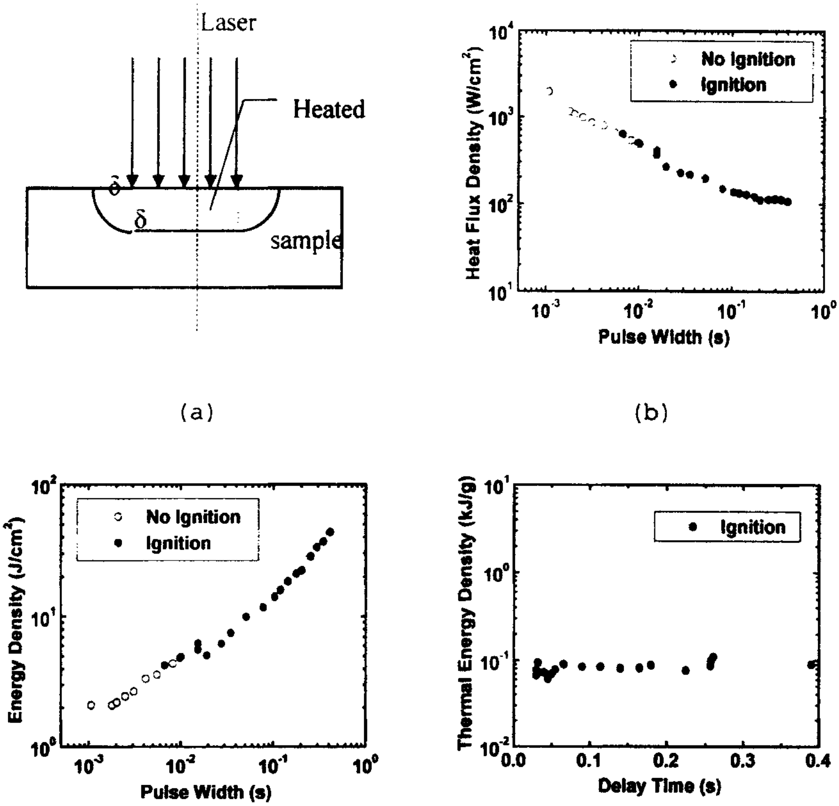
$$e = Q/m = Q/\rho V$$

where Q is the thermal energy absorbed by the sample. The experimental data and estimation results are indicated in TABLE 6(b). Ref. [3] regarded heat flux density and energy density as criteria. Using these criteria, it is very difficult to find an ignition rule. The results are shown in TABLE 6(b), and FIGURE 3(b) and (c). If calculated thermal energy densities are regarded as a criterion, they are approximately a constant. This is shown in TABLE 6(b) and FIGURE 3(d).

TABLE 6(b)

Laser igniting PM

Pulse width (s)	Heat flux (W)	Energy (J)	Time to ignition (s)	Heat flux density (W/cm^2)	Energy density (J/cm^2)	e (kJ/g)
0.00107	54.6	0.058	—	1970	2.09	—
0.00181	32.3	0.058	—	1160	2.09	—
0.00204	29.7	0.061	—	1070	2.20	—
0.00251	27.4	0.068	—	987	2.45	—
0.00311	23.9	0.074	—	861	2.67	—
0.00419	22.1	0.093	—	796	3.35	—
0.00553	18.2	0.1	—	656	3.60	—
0.0067	17.63	0.118	0.03	635	4.25	0.067
0.00824	14.8	0.122	—	533	4.39	—
0.0098	13.8	0.135	0.031	497	4.86	0.075
0.0101	13.56	0.137	0.03	488	4.94	0.078
0.0154	10.1	0.156	0.04	364	5.62	0.073
0.0154	11.36	0.174	0.032	409	6.27	0.095
0.0193	7.32	0.141	0.045	264	5.08	0.061
0.0276	6.24	0.173	0.05	225	6.23	0.070
0.035	5.89	0.209	0.055	215	7.53	0.079
0.051	5.41	0.276	0.066	195	9.94	0.091
0.078	4.15	0.324	0.09	149	11.7	0.085
0.103	3.77	0.388	0.114	136	14.0	0.085
0.119	3.7	0.438	0.14	133	15.8	0.081
0.143	3.55	0.509	0.165	128	18.3	0.082
0.175	3.34	0.584	0.18	120	21.0	0.088
0.201	3.08	0.62	0.225	111	22.3	0.077
0.25	3.14	0.79	0.257	113	28.5	0.087
0.293	3.16	0.93	0.258	114	33.5	0.100
0.344	3.1	1.03	0.261	112	37.1	0.110
0.406	2.98	1.21	0.39	107	43.6	0.090



(a) (b)

(c) (d)

FIGURE 3

(a) Heated field of the sample, (b) Ignition heat flux density vs. pulse width, (c) Ignition energy density vs. pulse width, (d) Ignition thermal energy density vs. delay time

Laser Igniting RDX

Ostmark(1994), using a tunable 180W CW CO_2-laser (λ=9~11μm), measured the threshold ignition energy of RDX [10]. The radius of laser beam is R=0.9mm, and the tests were done under pressure 30atm. The sample of mass is m=300mg, density ρ=1.64g/cm^3(90%TMD), size Φ10mm×2.5mm, heat capacity c=1.13kJ/(kg·K), thermal conductivity K=0.2W/(m·K). In order to better interpret the experimental data, he plotted ignition energy vs. absorption depth, but he did not give a distinct explanation of the fitted straight line (see FIGURE 4(a)). We analyze again these data as follows.

Thermal energy density is

$$e = Q/\rho \cdot \{\pi/6 \cdot \delta \cdot [3(R+\delta)^2 + 3R^2 + \delta^2]\} .$$

The ignition delay time is

$$t = \delta^2 \rho c/K .$$

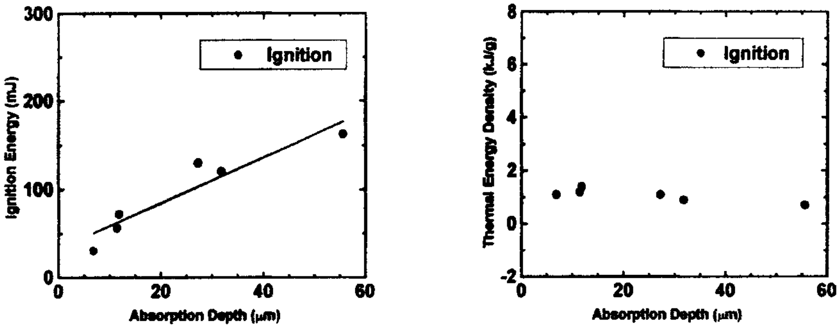
In spite of the fact that the absorption depths were different, the absorbed thermal energy densities are almost equal, see FIGURE 4(b). Based on TABLE 7, absorption depth δ, compared with the radius R of laser beam, may be neglected. Hence the heated fields are regard as the cylinders of radius R=0.9mm and height δ. The thermal energy density is given by the following relation

$$e = \frac{Q}{m} = \frac{Q}{\rho \pi R^2 \delta} = \frac{1}{\rho \pi R^2}\frac{Q}{\delta} = cons\tan t\frac{Q}{\delta}.$$

TABLE 7

Laser igniting RDX

Wavelength (μm)	Wavenumber (cm^{-1})	Absorption depth (μm)	Energy (mJ)	e (kJ/g)	Delay time (ms)
9.29	1076	55.6	162.9	0.7	28.6
9.50	1052	27.2	130.3	1.1	6.9
9.64	1037	11.8	72.2	1.4	1.3
10.27	973	31.8	120.8	0.9	9.4
10.59	944	11.4	56.3	1.2	1.2
10.76	929	6.8	30.7	1.1	0.4



(a)

(b)

FIGURE 4

(a) Threshold ignition energy vs. absorption depth for RDX, (b) Thermal energy density vs. absorption depth for RDX

The experimental data and estimation results are indicated in TABLE 7. Now we may explain distinctly the physics meaning of straight line in FIGURE 4(a). According to the above relation, the slope of straight line indicates that the thermal energy density is a constant.

Results

Based on the above magnitude order analyses of thermal energy density and delay time for energetic material ignition, the results are plotted in FIGURE 5. Since experimental ways are difference, the figures can only account for the approximately trend. When energetic materials ignited, the shorter is the delay time, the absorbed thermal energy density gets more. Rather surprisingly, no matter how the external stimuli and delay times change over the wide range (10^{-6}s~10^{4}s), the thermal energy density approximates to a constant. In light of the above estimation, the thermal energy density of energetic materials absorbing exits a minimum value. When the absorbed thermal energy density is more than it, energetic material may be ignited. We define the critical thermal energy density as the minimum thermal energy density absorbed by energetic materials when ignited.

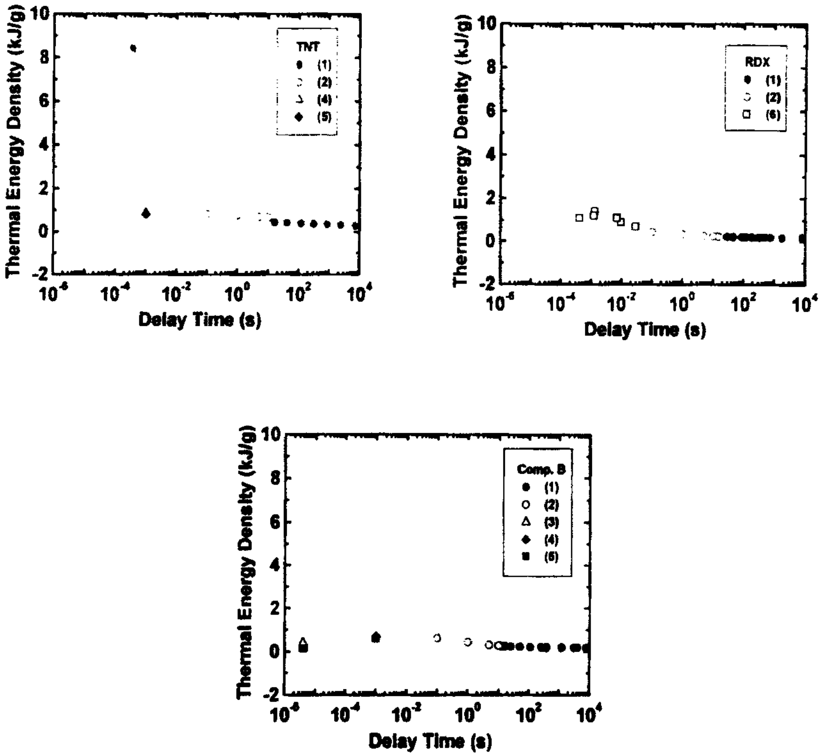


FIGURE 5

Order of magnitude estimates of thermal energy density vs. delay time. (1) One-Dimensional Time to Explosive, (2) Explosion Temperature, (3) Thermal Ignition with High Pressure, (4) Friction Ignition, (5) Shearing Ignition, (6)Laser Igniting RDX.

DISCUSSION

Comparison with the references

James (1996), to predict shock ignition thresholds, extended the critical energy criterion [11]. In the original criterion, the critical energy (E_c) was defined as the energy per unit area of the initial shock transferred into the explosive upon impact of a flyer plate. It is related to the shock parameters in the explosive by

$$E_c = pu\tau$$

where p was shock pressure, u was particle velocity, and τ was shock duration. His criterion was written as

$$\Sigma_c = E_c / 2\rho_0 w\tau$$

where ρ_0 was the ambient material density, w the shock velocity. In reality, Σ_c is the absorbed energy per unit mass of the initial shock transferred into the explosive upon impact of a flyer plate, namely it can be seen that Σ_c is a formulation of the critical thermal energy density under shock ignition conditions. The criterion, Σ_c, can be successfully applied to homogeneous explosives, e. g., Σ_c of molten TNT and nitromethane were 2.1MJ/kg and 2.5MJ/kg. From an order of magnitude point of view, the two values come close to the estimation results of critical thermal energy densities. But for the heterogeneous explosives, their values of Σ_c are smaller than the critical thermal energy densities in the paper. Here, we may give an explanation. For homogeneous explosives, under shock ignition conditions, the shock-induced unitary material was heated. For heterogeneous explosives, the shock-induced material was heated locally, then there exist some local higher temperature regions, namely so-called hot spots. In Ref [11], the behavior was still analogous to that for homogeneous explosives in that the total absorbed thermal energy was divided by the shocked-induced mass. If Ref [11] had considered the local effects, the values of Σ_c would also approximate to the critical thermal energy densities.

Tarzhanov et al (1996) were interested in the light absorption by PETN crystals when they researched on laser initiation [12]. The energy density estimated in the initiation spot equaled 1.16kJ/g. It can be shown that the datum is also consistent with the estimation data of the critical thermal energy densities.

Bond Energy

From another point of view, because the basic cause of ignition is rupture of atomic links in molecules of energetic materials, the stability of atomic groups in energetic materials remarkably affects their sensitivities. The energetic materials e. g. TNT($C_7H_5N_3O_6$), RDX($C_3H_6N_6O_6$), HMX($C_4H_8N_8O_8$) and the composition energetic materials made up of them are constituted by the elements of C, H, O, N. The molecules include weak bonds (bond energy ~50kcal/mol) and strong bonds (bond energy ~100kcal/mol). The values of bond energies and critical thermal energy densities are near. They are shown in TABLE 8.

TABLE 8

Common bond energy of energetic materials [9]

Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)	Bond	Bond energy (kcal/mol)
C-N	54	C-H	86	O=N	108
N-N	27	N-H	83	C=C	101
O-N	61	H-H	103	O=O	117
C-O	75	O-H	110	C=O	150
C-C	63	C=N	84	$C-NO_2$	240
O-O	35	N=N	80	$N-NO_2$	231

It is known from the ODTX and explosion temperature tests that the temperature rise only is below 500℃. In the two thermal decomposition tests [1,2], the estimated values of critical thermal energy densities are close to weak bond energies of energetic material molecules because the unstable atomic links are cut. In strong stimuli, e. g. detonation, the temperatures rise above 1000℃ and pressures of several tens of GPas are produced in their chemical action zone, then all the weak and strong bonds are ruptured, consequently the estimated values of critical thermal energy densities approach strong bond energies.

Activation Energy

The activation energy is one of the most important parameters on scaling reactive ability, therefore it is also taken for the ignition energy threshold of energetic materials. Activation energies (E) and estimated thermal energy densities (e) are listed in TABLE 9. In order to compare, E and e are expressed with two units (kcal/mol and kJ/g).

TABLE 9

Activation energies and critical thermal energy densities

	TNT	RDX	HMX	Comp. B
E(kcal/mol)	34.4	47.1	52.7	43.1
E(kJ/g)	0.63	0.89	0.74	0.80
e(kJ/g)	0.28~1.2	0.18~2.0	0.3~2.0	0.19~1.9
e(kcal/mol)	15.2~65.2	9.6~106.2	21.2~141.7	10.2~101.8

During the thermal decomposition of simpler gas phase nitryl compounds, the bonds of C-N, N-N, O-N, et al, rupture first. But for condensed energetic materials especially solid phase, the closer proximity of the molecules causes increased intermolecular interactions, and the chemical reactions can become much more complicated. Although the primary product is still NO_2, owing to effects of the molecule bonds, geometry and local chemical characters of condensed energetic materials, it is impossible that the primary values of activation energy is close to their relevant ones of C-N, N-N, O-N et al. In fact, activation energies are generally measured experimentally. The activation energy for explosives commonly range from 30.0kcal/mol to 60.0kcal/mol. Generally speaking, the smaller the activation energy the greater the sensitivity. So, activation energy may be regard as a standard for scaling sensitivity. It must be pointed out that not all energetic materials, due to various elements influencing the behavior, abide by the rule.

The thermal energy densities of energetic materials estimated above are of the same order of magnitude as atomic bond energies and activation energies. This is consistent with the idea that, in order to induce chemical reactions, energetic materials must absorb an adequate quantity of energy from outside to destroy atomic bonds or activate their molecules. The energy threshold may be expressed by a critical thermal energy density. By this token, the critical thermal energy density can be regarded as an ignition criterion. For any sensitivity tests of energetic materials, when the thermal energy density absorbed exceeds the threshold, chemical reaction is likely to take place. The critical thermal energy density may be taken for a characteristic parameter of energetic material ignition. If the estimation is correct, the critical thermal energy density will become an important characteristic parameter for scaling various sensitivities. It then becomes possible to rank the sensitivities of energetic materials under various stimuli.

CONCLUSIONS

In summary, the critical thermal density can be considered as a trigger energy for energetic materials ignition, and it may be regarded as an ignition criterion. It is a characteristic parameter that can reflect the ignition ability of energetic materials. From physical nature, it is the minimum ignition thermal energy density absorbed by energetic materials activated; from chemistry nature, it is the minimum thermal energy causing chemical bond rupture or molecule activation.

From a macroscopic point of view, ignition mainly rests with thermal energy absorbed from various stimulus forms. It is usually affected by following elements: initial temperature and pressure, chemical exothermic reaction and transport, characteristic geometrical scale and time.

If critical thermal energy densities of various energetic materials can be measured, they provide a quantitative single valued parameter that describes the sensitivity of energetic materials, and we may rank their sensitivities. However, it is noted that generally measuring the thermal energy density absorbed from energetic materials is very difficult.

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