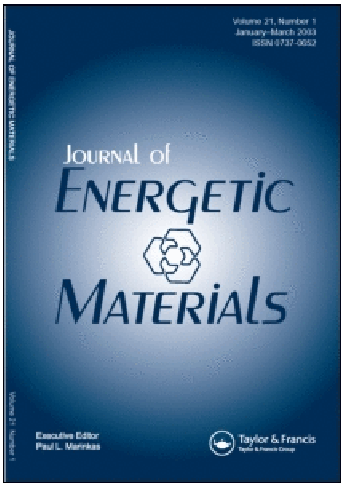

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article TARVER, CRAIG M.(2004) 'Chemical Kinetic Modeling of HMX and TATB Laser Ignition Tests', Journal of Energetic Materials, 22: 2, 93 — 107
To link to this Article: DOI: 10.1080/07370650490492842
URL: http://dx.doi.org/10.1080/07370650490492842

Energetic Materials, 22: 93–107, 2004

ISSN: 0737-0652 print
DOI: 10.1080/07370650490492842

Chemical Kinetic Modeling of HMX and TATB Laser Ignition Tests

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Recent high-power laser deposition experiments on octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) produced ignition times from milliseconds to seconds. Global chemical kinetic thermal decomposition models for HMX and TATB developed to predict thermal explosion experiments lasting seconds to days are applied to these laser ignition experimental data. Excellent agreement was obtained for TATB, while the calculated ignition times were longer than experiment for HMX at lower laser fluxes. Inclusion of HMX melting and faster reaction for liquid HMX in the HMX decomposition model improved the agreement with experiment at lower laser energies.

Keywords: HMX, TATB, decomposition, thermal

Introduction

Accident scenarios involving pressed solid high explosives include heating to thermal explosion, impact formation of localized ‘‘hot spots,’’ and shock compression of voids creating very hot regions [1]. Global chemical decomposition models have been developed to predict times to explosion and the location with in the explosive charge where runaway reaction first occurs [2–4]. These

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calculations are used as the bases for estimations of the violence of thermal explosions as functions of heating rate, confinement, damage, and porosity [5]. Because of the absence of experimental chemical kinetic data at higher temperatures, these models are also being used to estimate the critical conditions for "hot spot" ignition during impact and shock compression scenarios [6] and the growth rates of shock-induced hot spots during shock-to-detonation transition (SDT) processes [7]. They are currently being used to model shock initiation and detonation wave propagation in a grain-scale model [8] and in a statistical hot spot reactive flow model being developed in the thermal-mechanical-hydrodynamic coupled computer code ALE3D [9].

Recently Ali et al. [10] heated octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) pellets to thermal ignition using two CO_2 lasers. The measured times to explosion are in the second-to-millisecond regime, and the measured average ignition temperatures were 650 K for HMX and 708 K for TATB. These times to explosion are shorter than those that can be measured in most thermal explosion experiments, such as the One-Dimensional Time to Explosion (ODTX) apparatus [11]. Thus these rapidly heated laser ignition experiments represent an excellent test of the HMX and TATB global chemical decomposition models. This test helps determine whether these models, normalized to experimental data in the 453–593 K range, can be used for predictions of thermal response of HMX and TATB at higher temperatures, such as those occurring in impact and shock-induced hot spots. In this paper, the laser ignition experiments are briefly discussed. Then the global HMX and TATB chemical decomposition models are presented. The calculated times to ignition are then compared to the experimental measurements in the Results section. Finally, some conclusions are drawn, and some future research areas are identified.

Experimental

Ali et al. [10] used two different CO_2 lasers to heat 1 cm diameter by 6.4 mm thick pressed pellets of HMX and TATB to thermal ignition. The Edinburgh Instruments Ltd. PL-6 180 Watt laser has a rise time of approximately 2 ms. The PRC Corp. SL 1000 1000 Watt laser has a rise time of 0.6 ms. The laser beam profiles and the diagnostics used are fully discussed. For irradiances less than 60 W/cm^2, no differences were observed in the measured ignition delays using the two lasers under atmospheric conditions. TATB exhibited a single ignition time dependence over the entire range of laser fluxes, while the HMX data exhibited two distinct trends with a transition region of high scatter in the 50–100 W/cm^2 range. The ignition temperatures measured using fast response thermocouples did not change significantly for the range of irradiances used. Ali et al. [10] also included HMX laser ignition time data from other experimental studies that agreed well with their measurements. Various experimental details, uncertainties, and future experimental research were discussed.

Chemical Kinetic Decomposition Models for HMX and TATB

Three-to-five-step global chemical decomposition models have been developed for several solid high explosives. The HMX chemical decomposition model consists of four reactions and five chemical species. The reaction sequence is [4]

$$\text{Beta HMX} \longrightarrow \text{Delta HMX}, \tag{1}$$

$$\text{Delta HMX} \longrightarrow \text{Solid Intermediates}, \tag{2}$$

$$\begin{aligned}\text{Solid Intermediates} \longrightarrow\ & \text{Gaseous Intermediates} \\ & (CH_2O, N_2O, HCN, HNO_2, \text{etc.}),\end{aligned} \tag{3}$$

$$\text{GaseousIntermediates} \longrightarrow \text{FinalProducts}(CO_2, H_2O, N_2, CO, C, \text{etc.}). \tag{4}$$

The major pathways for HMX decomposition have been reviewed by Behrens et al. [12]. The solid-solid beta-to-delta phase transition is treated as a separate reaction in Equation (1) [4], whereas previously it had been included with Equation (2) as one overall endothermic process [2]. Equation (2) describes the initial ring and bond breaking endothermic step(s). HMX decomposition is known to produce as the main intermediate products CH_2O plus N_2O under some temperature and pressure conditions and HCN plus HNO_2 under other conditions [12]. Equation (3) is slightly exothermic, and thus most of HMX's chemical energy is released during the gas phase formation of the final stable reaction products by second-order gas phase reactions in Equation (4).

The TATB model is based on less chemical kinetic data than the HMX model and has not changed recently [5]. It consists of three reactions and four species. The TATB sequence is

$$\text{TATB} \longrightarrow \text{Solid Intermediate A} + H_2O, \tag{5}$$

$$\text{Solid Intermediate A} \longrightarrow \text{Solid Intermediate B} + \text{Gases}, \tag{6}$$

$$\text{Solid Intermediate B} \longrightarrow \text{Final Gaseous Products}. \tag{7}$$

It is known that TATB reacts mainly in the condensed phase and that all of the possible H_2O molecules can be formed during extremely slow heating leaving $C_6H_6O_3$ behind [5]. At faster heating rates, the first two reactions, Equations (5) and (6), are assumed to be endothermic steps that eliminate H_2O and then other intermediate gaseous products, such as NO. The third reaction is assumed to be an exothermic, second-order reaction. Some kinetic data are available and used for the rates of the three reactions [5]. In the ODTX apparatus, TATB-based explosives exhibit essentially the same times to explosion under heavy confinement and with no confinement [2, 5]. Thus it is likely that gas phase reactions do not dominate the chemical energy release process in TATB as they do in HMX.

Table 1 lists the thermal property and reaction rate parameters for the HMX decomposition model, and Table 2 lists those for TATB. Both models have been used to calculate times to and locations of thermal explosion for the ODTX and other thermal experiments with various heating rates, degrees of confinement, and geometries [2–5]. These models are used directly to model the laser ignition experiments of Ali et al. [10] by placing a time-dependent heat flux boundary condition on the top of the pellet. The experimental uncertainties in the laser flux reaching the solid explosive surface discussed by Ali et al. [10] are not considered in these two-dimensional calculations using the Chemical TOPAZ heat transfer code [13]. The calculated times to thermal ignition for HMX and TATB are compared to experiment in the next section.

Results

The times to ignition for laser-heated HMX and TATB are calculated using the Chemical TOPAZ code with very fine zoning to ensure that the calculations have converged to a consistent answer. For these 0.64 cm thick pellets, 320 zones are sufficient. After the appropriate laser pulse rise time, a constant flux boundary condition is applied to the pellet surface. The HMX and TATB chemical decomposition models in Tables 1 and 2 agree well with slower heating rate and longer time-to-ignition thermal explosion experiments. Figure 1 shows the comparison between the measured and calculated times to ignition as various laser irradiances for HMX. Figure 2 shows a similar comparison for TATB. Both thermal decomposition models agree well with the laser ignition data. The HMX model overpredicts the times to ignition at lower laser fluxes and underpredicts those for high laser fluxes. The TATB model predicts the measured times to ignition very well over the entire range of irradiances. The TATB model is based on less experimental chemical kinetic and thermal explosion data but appears to agree with this high-temperature, short-time-duration, laser-driven time-to-ignition data better than the HMX model does.

One reason for the higher calculated times to explosion for HMX may be that HMX melts at 558 K, and the average ignition in these experiments is 650 K. HMX melting was not included in the HMX decomposition model for slower thermal events,

Table 1
Thermal and reaction rate parameters for HMX model

	Beta HMX	Delta HMX	Solid intermediate	Intermediate gases	Final gases
1. Initial density (g/cm^3)	1.85	1.70			
2. Heat capacity (cal/g-K) at:					
298 K	0.24	0.24	0.22	0.24	0.27
373	0.30	0.30	0.27	0.26	0.28
433	0.34	0.34	0.31	0.27	0.28
563	0.40	0.40	0.36	0.29	0.29
623	0.46	0.46	0.42	0.31	0.30
773	0.55	0.55	0.50	0.35	0.31
>1273	0.55	0.55	0.50	0.42	0.35
3. Thermal conductivity (cal/cm-g-K) at:					
298	1.28×10^{-3}	1.18×10^{-3}	1.08×10^{-3}	9.80×10^{-4}	1.0×10^{-4}
373	1.09×10^{-3}	1.00×10^{-3}	9.20×10^{-4}	8.8×10^{-4}	1.0×10^{-4}
433	1.02×10^{-3}	9.20×10^{-4}	8.30×10^{-4}	8.3×10^{-4}	1.0×10^{-4}
563	8.15×10^{-4}	8.15×10^{-4}	8.15×10^{-4}	8.15×10^{-4}	1.0×10^{-4}
623	7.50×10^{-4}	7.50×10^{-4}	7.50×10^{-4}	7.5×10^{-4}	1.0×10^{-4}

773	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
>1273	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
4. Heat of formation (cal/g)	$+61.0$	$+71.0$	$+131.0$	-2.0	-1339.0
5. Reaction rate para-meters $\mathrm{Na}^x qZe^{-E/RT}$ (where Na is mass fraction)					

Reaction	ln Z	E(kcal/mol)	Reaction order ×	Heat of reaction q(cal/g)
1	48.13	48.47	1	+10.0
2	48.7	52.70	1	+60.0
3	37.8	44.30	1	−133.0
4	28.1	34.10	2	−1337.0

Table 2
Thermal and reaction rate parameters for the TATB model

	TATB	Solid intermediate A	Solid intermediate B	Gaseous products
1. Initial density (g/cm^3) = 1.835 g/cm^3				
2. Heat capacity (cal/g-K) at:				
298 K	0.26	0.24	0.26	0.26
433	0.36	0.33	0.28	0.28
573	0.45	0.39	0.29	0.29
623	0.47	0.41	0.30	0.30
673	0.49	0.42	0.30	0.30
773	0.54	0.48	0.35	0.35
>1273	0.54	0.48	0.35	0.35
3. Thermal conductivity (cal/cm-g-K) at:				
298 K	2.10×10^{-3}	1.05×10^{-3}	5.00×10^{-4}	1.00×10^{-4}
433	1.56×10^{-3}	7.80×10^{-4}	3.90×10^{-4}	1.00×10^{-4}
573	1.10×10^{-3}	5.50×10^{-4}	2.70×10^{-4}	1.00×10^{-4}
623	1.00×10^{-3}	5.00×10^{-4}	2.50×10^{-4}	1.00×10^{-4}
673	1.00×10^{-3}	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}

773	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}
>1273	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}
4. Heat of formation (cal/g)				
	−142.7	−92.7	+42.7	−742.7
5. Reaction rate parameters $\mathrm{Na}^x qZe^{-ERT}$ (where Na is mass fraction)				

Reaction	ln Z	E(kcal/mol)	Reaction order ×	Heat of reaction q(cal/g)
1	48.0	60.0	1	+50.0
2	29.8	42.0	1	+50.0
3	26.8	33.8	2	−700.0

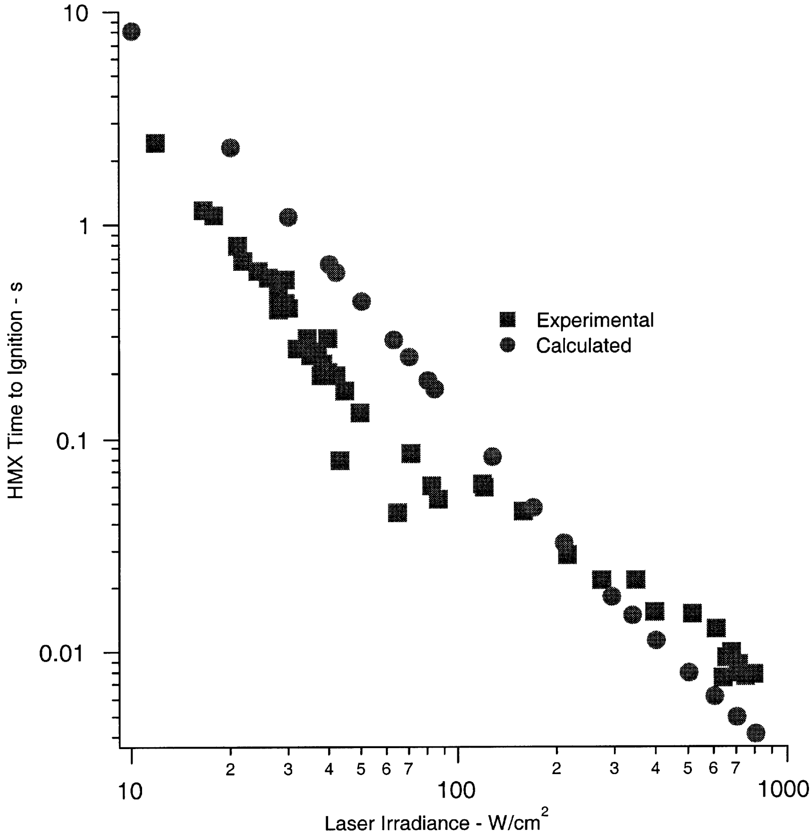

Figure 1. Experimental and calculated ignition times vs. laser irradiance for HMX.

because almost all of the data are taken at temperatures below the melting point [4]. Inclusion of the endothermic melting process increases the HMX times to explosion slightly, but it is known that organic solid explosives generally react faster in the liquid phase than in the solid phase, because of the greater mobility of liquids and intermediate products [12]. The modern ODTX apparatus [11] has been used to measure three times to thermal explosion for HMX at temperatures exceeding the melting point. These three times to thermal explosion at the ODTX constant temperatures are listed in Table 3. The new ODTX closes

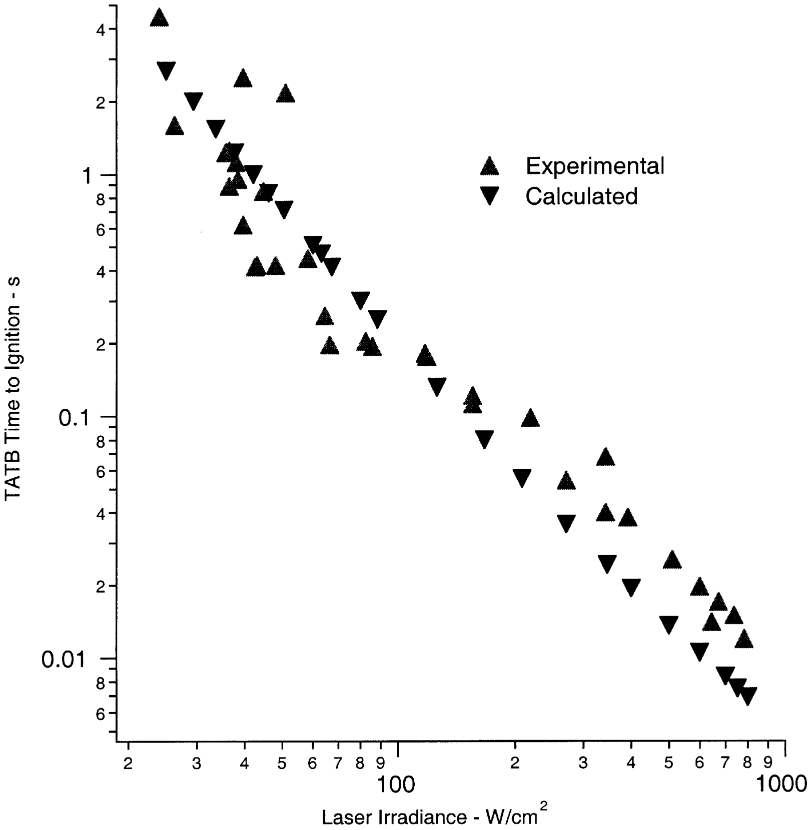

Figure 2. Experimental and calculated ignition times vs. laser irradiance for TATB.

and seals in 1–2 s [11], so these measured times to explosion are meaningful. The three calculated times to explosion using the HMX decomposition parameters listed in Table 1 are shown in Table 3 and are considerably higher than experiment. Incorporating HMX melting as a 56.4 cal/g endotherm [14] between 557 and 559 K and increasing the natural logs of the frequency factors by 4 and decreasing the activation energies by 4 kcal/m for reactions 2, 3, and 4 results in the shorter ODTX times to explosion listed in Table 3. Applying these faster reaction rates to the measured HMX laser ignition times at various irradiation levels yields

Table 3
HMX model including melting and faster rates

Reaction	ln Z	E(kcal/mol)	Reaction order ×	Heat of reaction q(cal/q)
1	48.13	48.47	1	+10.0
2	52.7	48.70	1	+60.0
3	41.8	40.30	1	−133.0
4	32.1	30.12	2	−1337.0
ODTX Temp.	Experimental time (s)	Calculated regular rates (s)	Calculated faster rates (s)	
573.05	3.9	8.7286	3.8184	
563.25	5.1	13.892	5.1223	
558.65	7.8	17.530	6.0885	

Note: Heat of fusion = 56.4 cal/g at 558 K. [14]

the time-to-explosion curve shown in Figure 3. The resulting calculated ignition times are closer to the experimental times at lower laser fluxes but farther from experiment at high fluxes.

Liau and Lyman [15] calculated the times to ignition for the HMX laser experiments using a chemical kinetics scheme involving 45 species and 232 gas phase reactions. Their calculated HMX ignition times agreed well with experiment, except in the lower flux range, where their model also gave a steeper slope than observed experimentally. When the gas plume produced at the HMX surface was allowed to expand radially to eight times the original area 2 cm from the HMX surface, their calculated ignition times at lower laser fluxes agreed more closely with experiment.

Conclusions

HMX and TATB global chemical decomposition mechanisms derived from thermal explosion data in the seconds-to-days

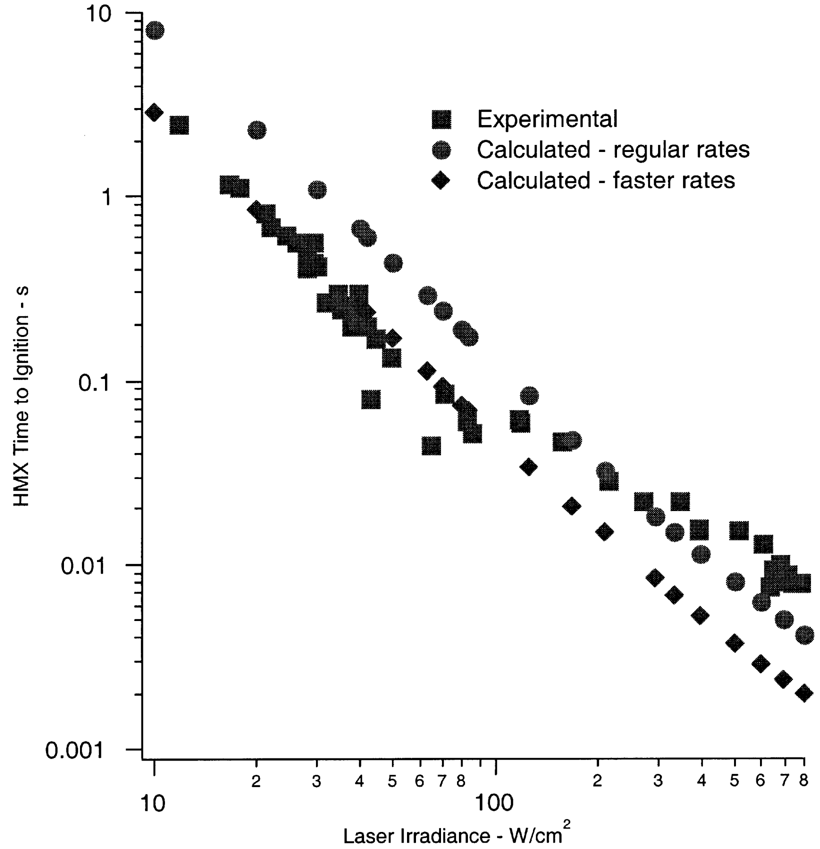

Figure 3. HMX times to ignition: experimental and calculated with regular and faster reaction rates.

time frame are applied to recent high-power laser ignition experiments that produced times to ignition in the millisecond-to-second time frame. The overall agreement between the measured and calculated times to ignition is good, especially for TATB. This agreement is certainly reasonable enough for these models to be used to estimate critical temperatures for various hot spot sizes formed during impact and shock initiation processes until such hot spot temperatures and dimensions can be measured experimentally [6–9]. The close agreement with the TATB laser ignition times may imply that gas phase absorption of laser energy is not important for TATB, which agrees with previous conclusions that most of the preexplosion chemistry of TATB occurs in the condensed phase. On the other hand, HMX decomposition is believed to be very dependent on gas phase and HMX surface reactions [12, 15]. Therefore gaseous products of HMX decomposition leaving the irradiated surface may absorb significant amounts of laser energy, as discussed by Liau and Lyman [15]. Ali et al. [10] plan to expose HMX and TATB to high laser powers, resulting in faster ignitions that will further test the decomposition models. Chemical kinetic reaction rate experiments on liquid HMX are needed to shed identify increases in reaction rates upon melting.

Acknowledgments

The author would like to thank Arif Ali of the Los Alamos National Laboratory for providing a printout of his experimental data. This work was performed under the auspices of the United States Department of Energy by the Lawrence Livermore National Laboratory under contract no. W-7405-ENG-48.

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