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Development and Validation of Detailed Finite-Rate Chemical Kinetics Mechanisms for Modeling the Combustion of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazocane—Hydroxyl-Terminated Polybutadiene (HMX-HTPB) Composites

by Chiung-Chu Chen, Jeffrey D Veals, and Michael J McQuaid

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14. ABSTRACT The trial mechanism method (TMM) was employed to reduce a large (3825 reaction-1017 species) finite-rate chemical kinetics mechanism for modeling the gas-phase combustion associated with the deflagration of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane—hydroxyl-terminated polybutadiene (HMX-HTPB) composites. Targeting the creation of skeletal mechanisms for use in a 2-D laminate computational fluid dynamics model of such phenomena, the TMM's screening protocol compared results from solutions to homogeneous reactor problems. The candidate selected for the application comprised 135 reactions and 117 species. Its selection was based in part on burning rate predictions for pure HMX produced with a 1-D steady laminar (CYCLOPS) deflagration model into which it was integrated. Beyond providing evidence for the candidate's validity for the intended application, results produced with it indicated that HMX's burning rate at a given pressure was relatively independent of the temperature of the burning surface. As such, they call into question using representations for the condensed-phase-to-gas-phase conversion process that are formulated solely on that basis. The CYCLOPS model's predictions for the burning rate of a hypothetical homogeneous HMX-HTPB mixture provided additional evidence for the candidate's validity for the application. All the inputs needed to construct the candidate are provided in an addendum (ARL-TN-1061) to this report.					
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1. Introduction

The energetic material 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) is the primary ingredient in many plastic-bonded explosives (Dattelbaum and Stevens 2008), and there has been interest in exploiting the high impetus and specific impulse of HMX–polymer composites as propellants for rocket and gun propulsion systems (Cohen and Price 1975; Moy 1975; Kumar and Strand 1977; Beckstead and McCarty 1982; Blomshield 1989; Duterque and Lengelle 1990; Zenin 1998; Lengelle et al. 2002; Naya and Kohga 2013). However, the pressure (P) dependence of their burning/regression rates (r) is higher than suitable for either application. When expressed per Vieille’s law,

$$r = AP^n, \tag{1}$$

where A and n are constants, they exhibit pressure exponents (n) near 1.0 (or more) over applicable P ranges, and therefore have an inherent potential for amplifying combustion instabilities. In rocket motors, this potential can lead to catastrophic failures, making them completely unsuitable for that application. Such burning-rate behavior has less potential to fail guns catastrophically. However, it can negatively impact ballistic efficiency and reproducibility, making them undesirable for that application as well. Nevertheless, interested in elucidating via modeling the mechanisms that underlie the change in the P dependence of the burning rates of rocket propellants formulated with ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB), we became interested in modeling the deflagration of HMX–HTPB composites as well (Nusca 2014).

When the burning rates of AP–HTPB composite propellants are expressed per Vieille’s law, values of n tend to be considerably less than 1 at pressures up to about 150 atm (2200 psi), then increase significantly at higher pressures. (The change in n observed near 150 atm is often referred to as an exponent break.) As such, this phenomenon constitutes an impediment to a (theoretically) straightforward approach to improving a rocket motor’s performance, namely, increasing its operating pressure. Means for moving breaks to higher pressures have therefore been sought. To advance such efforts, models were developed and applied to understand the factors that control their burning rates. However, constructs formulated prior to about (the year) 2000 included a fair amount of empiricism, and a consensus with respect to the mechanism(s) causing exponent breaks failed to emerge (Atwood et al. 1999; Beckstead 2006).

Believing models employing a detailed* finite-rate chemical kinetics mechanism developed using state-of-the-art computational methods might shed new light on the phenomenon, we developed and applied them (Chen and McQuaid 2014, 2015). Integrating a skeletal version of a comprehensive detailed mechanism into a 1-D steady laminar (CYCLOPS) burning-rate predictor, we calculated AP's burning rate at pressures from 2 to 2,000 atm (McQuaid and Chen 2014). Burning rates at pressures up to 150 atm were well reproduced. However, a trend to lower (local) values of n observed in this range extended to 2,000 atm, indicating that gas-phase chemical kinetics alone was not sufficient to explain exponent breaks. That prompted us to revisit the literature on the subject and garner an appreciation of a hypothesis (and supporting empirically based model) that thermo-mechanically induced AP particle break-up plays a role (Irwin et al. 1963). Therefore, a submodel to simulate that phenomenon was incorporated into a 2-D laminate computational fluid dynamics (CFD) model for simulating AP-HTPB deflagration (Nusca 2014). In the course of developing that model, Nusca identified crevice formation between AP particles and the binder as another mechanism with the potential to influence AP-HTPB burning rates. He therefore developed and included in his model a submodel for simulating that as well.

With cracking and crevice formation submodels incorporated into the 2-D laminate CFD model, the measured burning rates of AP-HTPB composites could be well reproduced over the entire pressure range of interest, supporting the hypothesis that these phenomena were important. However, the submodels for cracking and crevice formation included parameters whose values were not derived from first principles. Rather, they were specified to obtain said agreement. The effort to model the deflagration of HMX-HTPB composites was undertaken in the hope of developing and validating physics-based cracking and crevice formation submodels.

A fair number of modeling studies of HMX and/or HMX-HTPB composite deflagration have been published. A study by Hatch (1987) is the first (of which we are aware) in which a detailed mechanism was employed to model the deflagration of HMX. Hatch constructed the mechanism from data he found in the open

*In publications pertaining to energetic material combustion modeling, "detailed mechanism" is often employed as shorthand for "network comprising atoms and molecules connected by elementary reactions". The expression was/is convenient for discussions in which one wishes to distinguish between such mechanisms and the "chemically non-specific mechanisms" that were employed in the earliest models in the discipline (Miller and Anderson 2000; Beckstead et al. 2007). Since the latter are still employed and/or referenced, its usage retains some currency, and it was the reason for using it in this report. However, unqualified, it groups detailed mechanisms developed and employed in the 1980s and 1990s with today's state-of-the-art mechanisms, and that could be misleading. Facilitated by increases in computing power and advances in computational methods, today's mechanisms enable investigations of processes near burning surfaces that are far beyond the ken of their forebears.

literature. It comprised 77 elementary reactions and 25 chemical species. None of the species had more than two multi-electron (non-hydrogen) atoms. To calculate the mass flux ($\dot{m}$) of the condensed-phase-to-gas-phase conversion process, he employed (what was in essence) a pyrolysis law,

$$\dot{m} = A \exp\left(-\frac{B}{RT^0}\right) \quad (2)$$

where A and B are constants, R is the universal gas constant, and T^0 is the temperature of the burning surface. Several different nascent product sets (comprising species in the chemical kinetics mechanism) were specified. Calculated burning rates ($r = \dot{m}/\rho_c$, where ρ_c is the density of the condensed phase) were within a factor of 2.5 of measured values, and the trend observed in their pressure-dependence was well reproduced. However, because the mechanism bypassed steps in HMX’s decomposition, the model’s capacity to elucidate the combustion chemistry (and therefore dynamics) near the burning surface was suspect. (For an appreciation of the differences in the results produced by a “small-molecule” mechanism such as that employed by Hatch and a mechanism that includes steps for the decomposition of a large parent such as the one employed for this effort, see Chen et al. [2019].)

A more comprehensive mechanism for modeling HMX’s decomposition was later assembled by Prasad et al. (1998). Comprising 228 reactions and 48 species, it was built by adding reactions to a mechanism they had constructed to model the combustion of 1,3,5-trinitro-1,3,5-triazinane (RDX) (Prasad et al. 1997). Among the additions were reactions for gas-phase HMX decomposing to large daughters (HMXR and HMXRO). Employing this mechanism in a 1-D multiphase model that they referred to as an “eigenvalue method”, Prasad et al. obtained good agreement between calculated and measured $r(P)$ values at pressures from 1 to 90 atm.

Despite the successes achieved with the mechanism–model combination developed by Prasad et al., studies of the decomposition of RDX and HMX based on quantum mechanics-based electronic structure methods suggested their mechanism could be improved. Chakraborty et al. (2001) and Zhang et al. (2003) characterized a large number of nitrogen dioxide (NO_2) and nitrous acid (HONO) elimination channels for large intermediates considered likely to be produced by HMX’s decomposition, and Zhang et al. employed transition state theory to parameterize rate coefficient formulae for the paths they characterized. However, we could find no published modeling studies of HMX’s deflagration that were based on mechanisms that included these improvements, and thus establish their impact. We were also unable to find any detailed mechanism for representing the gas-phase combustion chemistry associated with the deflagration of HMX–HTPB composites.

To address these issues, we built a comprehensive mechanism for modeling HMX–HTPB combustion. A summary of this mechanism’s development was recently presented (Veals et al. 2020). Briefly, Zhang et al.’s and Chakraborty et al.’s results were employed as starting points for building a mechanism for modeling the combustion of pure HMX. We extended their results by postulating and characterizing additional bimolecular reactions we thought might be important in its decomposition based on our experience in developing mechanisms for other systems. In addition, we employed models considered more reliable than the ones they employed to recalculate the structures, normal modes, and energies of stationary points of the pathways they had characterized. These data were employed to calculate thermodynamic properties for stationary point structures and rate coefficients for elementary reactions. To this mechanism, we added a mechanism constructed to model the combustion of HTPB when it is oxidized by red fuming nitric acid (RFNA) (Chen and McQuaid 2009, 2010). Formulae for computing rate coefficients for reactions needed to integrate the two mechanisms were also parameterized. In all, the full HMX–HTPB mechanism comprised 3817 reactions and 1017 species.

The primary objective of the effort summarized in this report was to create skeletal versions of the full HMX–HTPB mechanism that would reasonably mimic it within the parameter space relevant to the deflagration of HMX–HTPB composites at pressures from 5 to 700 atm. The trial mechanism method (TMM) was employed for that purpose (Kotlar 2010; McQuaid 2013; Chen and McQuaid 2016). Formulating and applying a screening protocol based on comparing results from solutions to homogeneous reactor (HR) problems, we found that the full mechanism could not be reduced to the targeted maximum size (120 reactions and 120 species) when the protocol enforced standards of agreement similar to those employed for many prior efforts. Informed by a recent study of the burning rates of nitroglycerine (NG)-additive mixtures (Chen et al. 2019), the standards of agreement for some of the parameters were relaxed. The rationale for deviations from past practice are discussed.

Post-reduction analyses were conducted to confirm candidates’ potentials to mimic the full mechanism in the intended application. Results from HR simulations that were the basis for mechanism reduction and candidate selection are presented and discussed. In addition, we formulated and employed a CYCLOPS model to predict burning rates for pure HMX and a hypothetical homogeneous HMX–HTPB formulation. Beyond providing the sought confirmation, those results proved interesting in their own right. In particular, they indicated that pure HMX’s burning rate at a given P is relatively independent of T^0 . Pertinent to formulating an expression for calculating the mass flux of the condensed-phase-to-gas-phase

conversion process in the 2-D laminate CFD model, the evidence is presented and discussed.

Of the candidates with the potential to be a submodel for the 2-D laminate CFD model, the one considered the best compromise between size and ability to mimic the full mechanism within the delineated parameter space comprised 135 reactions and 117 species. It is referred to hereafter as E10d. All the inputs needed to construct it are provided in an addendum to this report (Chen et al. 2021).

2. Computational Methods

2.1 Trial Mechanism Method

More-complete descriptions of the TMM are given elsewhere (Kotlar 2010; McQuaid 2013). Basic screening protocol steps include the following:

- Randomly ordering the starting mechanism's reactions.
- Sequentially eliminating (single) reactions from it on a trial basis.
- For each elimination, solving a canonical combustion problem (or problems) with the trial mechanism created by the elimination.
- Permanently eliminating a reaction if changes in the values of selected parameters of the solution(s) do not exceed specified criteria.

A species is eliminated when all reactions involving it are eliminated. Specifics of the screening protocols employed for this effort were as follows.

2.1.1 Homogeneous Reactor Simulations

While there are many combustion problem types that could be imagined as being bases for a TMM screening protocol, when this effort was started (in July 2018), only closed-system, adiabatic HR problems (as prescribed by SENKIN [Lutz et al. 1988]) had been employed by our group. Being the simplest of the CHEMKIN canon to formulate and solve, they were employed for the original development and application of the TMM (Kotlar 2010; McQuaid 2013). Moreover, prior to a recent effort (McQuaid 2020), there had been no compelling reason to formulate screening protocols based on problems that were more complex. In short, HR-based screening protocols were able to produce skeletal mechanisms with targeted sizes for all applications for which they were formulated, and evidence suggesting the skeletal mechanisms produced poor results in the applications of interest was not observed. (The use of this approach to create skeletal mechanisms for modeling the deflagration of AP-HTPB composites is one example [Nusca 2014].) Thus, we had

reason to expect that solutions to HR problems would be a suitable basis for reducing the full HMX–HTPB mechanism for modeling HMX–HTPB composite deflagration.

The HR model implemented by the screening protocol was constructed using subroutines in a pre-commercial CHEMKIN-III library (Kee et al. 2002). The governing equations corresponded to those for a closed adiabatic system whose pressure does not vary (CONP). Solutions were obtained with DASPK (Li and Petzold 2000). Table 1 shows the values of some input parameters for the sets of HR-CONP problems employed for the protocols. Bases for them and other important parameters were as follows.

Table 1 Screening protocol summaries

Set	Starting mech. size (# rxn-# spec)	Sim.	P^0 (atm)	T^0 (K)	Maximum acceptable deviation (MAD) protocol ^a			# ^b	Smallest candidate(s) (# rxn-# spec)
					1 st peak	2 nd peak	ΔT_f		
A	3784-967	1	10	710	1/1/10	1/1/10	1/1/10	40	156-126 (A21)
		2	100	910	1/1/10	1/1/10	1/1/10		
		3	1000	1280	1/1/10	1/1/10	1/1/10		
B	156-126	1	10	710	10/1/20	10/1/20	10/1/20	10	134-114 (B01)
		2	100	910	10/1/20	10/1/20	10/1/20		
		3	1000	1280	10/1/20	10/1/20	10/1/20		
C	156-126	1	10	710	10/0/10	11/1/20	11/1/20	10	146-122 (C07)
		2	100	910	10/0/10	11/1/20	11/1/20		
		3	1000	1280	10/0/10	11/1/20	11/1/20		
D	3199-825	1	10	715	1/1/10	1/2/19	1/1.5/14.5	40	143-124 (D02)
		2	100	780	1/1/10	1/2/19	1/1.5/14.5		
		3	700	835	1/1/10	1/2/19	1/1.5/14.5		
E	143-124	1	10	715	10/0/10	20/1/25	20/1/25	10	133-117 (E10a)
		2	100	780	10/0/10	20/1/25	20/1/25		134-117 (E10b)
		3	700	835	10/0/10	20/1/25	20/1/25		134-117 (E10c) 135-117 (E10d)
F	3199-825	1	10	715	1/1/10	2.5/2.5/25	2.5/2.5/25	80	127-128 (F09)
		2	100	780	1/1/10	2.5/2.5/25	2.5/2.5/25		
		3	700	835	1/1/10	2.5/2.5/25	2.5/2.5/25		
G	3199-825	1	10	715	1/1/10	2.5/2.5/25	1/1/10	40	137-138 (G04)
		2	100	780	1/1/10	2.5/2.5/25	1/1/10		
		3	700	835	1/1/10	2.5/2.5/25	1/1/10		

^aThe first number indicates the initial MAD, the second number indicates the relaxation interval, and the last number indicates the maximum MAD allowed. For example, for the parameters characterizing the two main local maxima/peaks in $\dot{q}_{m/v}(t)$ histories, 1/1/10 indicates the MADs were $\pm 1\%$ for the first pass, subsequently relaxed (collectively) in $\pm 1\%$ intervals, and allowed to reach $\pm 10\%$ (maximum). Similarly, for ΔT_f 1/1/10 indicates the MAD was ± 1 K for the first pass, subsequently relaxed (collectively with the MADs for the $\dot{q}_{m/v}(t)$ maxima) in ± 1 K intervals, and allowed to reach ± 10 K (maximum).

^bNumber of different reaction orderings processed. Screening at the maximum MADs was not performed in all cases.

2.1.1.1 Starting Reactants

The problems' starting chemical compositions ($\{X_k\}$, where X_k is the mole fraction of species k) were chosen to reflect expectations for the nascent products of the condensed-phase-to-gas-phase conversion process of the individual ingredients: HMX and HTPB. Despite suggestions that condensed-phase reactions play a role in the deflagration of HMX (Sinditskii et al. 2009), our success in reproducing the burning rates of methyl nitrate (McQuaid and Chen 2013), NG (Chen et al. 2019), and AP (McQuaid and Chen 2014) with CYCLOPS models in which the gas-phase-to-condensed-phase conversion process was modeled as a simple phase change prompted us to employ that paradigm for this effort. For HTPB, we chose a (single) relatively large hydrocarbon ($C_{20}H_{32}$) that had the same ratio of cis/trans/vinyl butadiene substructures as R45M. Labeled EODT, it (and a mechanism to decompose it) was originally proposed as the parent molecule for a model of HTPB's combustion in a hybrid rocket motor (Chen and McQuaid 2009, 2010). Toward validating the paradigm, it was employed as a basis for simulating HTPB's pyrolysis in thermogravimetric analysis experiments, and calculated rate coefficients proved to be in reasonable agreement with measured values (Chen and McQuaid 2009). On that basis, EODT was selected as the nascent product of HTPB's decomposition in an AP-HTPB deflagration model (Chen and McQuaid 2016), and the paradigm proved to have merit in that application as well. It was therefore a natural selection for this effort.

2.1.1.2 Initial Reactant Concentrations

In the combustion of HMX-HTPB composites, there are regions near the surface that are very rich in the daughters of HTPB's pyrolysis and others that are rich in the daughters of HMX's decomposition. As such, the probability that the screening protocol would produce candidates that are valid for this range of compositions would have increased if it included simulations with starting compositions that ranged from 100% HMX to 100% EODT. However, given the size of the full mechanism and the competing need/desire to perform simulations at several different pressures, that was not practical (in a straightforward and economical manner). Therefore, based on our experience in reducing the AP-HTPB mechanism (Chen and McQuaid 2016), where the same issue had to be addressed, we decided to employ only one starting composition (76.8 mol% HMX–21.9 mol% EODT). It corresponded to the mass fractions (Y_k) of the ingredients in the composite to be modeled by Nusca (2018): 80 wt% HMX–20 wt% HTPB (80:20 HMX-HTPB).

2.1.1.3 Pressures

For the initial set of TMM reductions that were submitted, the screening protocol included three HR-CONP problems: one at 10 atm, one at 100 atm, and one at 1000 atm. The simulation at 1000 atm was chosen to correspond to the high end of measured $r(P)$ data for pure HMX that was aggregated by Sinditskii et al. (2009). (Although the spacing of these selections may seem odd, on a traditional log-log plot of r vs. P , 10, 100, and 1000 atm are equally spaced.) When that set failed to produce any candidates with 120 or fewer reactions and 120 or fewer species, we reviewed the range of conditions over which the reduced mechanism was expected to mimic the full mechanism, hoping it, and thereby candidate sizes, could be reduced. Apprised of the situation, Nusca (2018) informed us that 700 atm was the highest P he planned to model. Therefore, in subsequent reduction protocols, that value was employed instead of 1000 atm.

2.1.1.4 Initial Temperatures

Wanting the initial temperatures (T_0) of the HR-CONP problems to correspond to the temperatures at the surface of a burning HMX–HTPB composite (T^0) at each P , we initially estimated them by coupling a (general) nitramine-binder pyrolysis law derived by Miller (2003) ($A = 2004 \text{ g/cm}^2\text{s}$, $B = 11,827 \text{ cal/mol}$) and the measured $r(P)$ data for the deflagration of pure HMX that was aggregated by Sinditskii et al. (2009).^{*} (Miller derived his law on the basis of measured data reported by Zenin [1998, 2000, 2002].) They were 710 K at 10 atm, 864 K at 100 atm, and 1280 K at 1000 atm. However, when the candidates produced by those selections were employed to calculate r values for pure HMX, the CYCLOPS model predicted that T^0 would be 715 K at 10 atm, 825 K at 100 atm, and 900 K at 1000 atm (see Section 3.4.). Therefore, for the next batch of reductions, the T_0 were set equal to these values. The T^0 predicted by the burning-rate calculations performed with candidates produced on that basis proved to be similar to the values specified for

^{*}In retrospect, the rationale for this approach to establishing T_0 was (somewhat) flawed. Representing the condensed-phase-to-gas-phase conversion process in the CYCLOPS framework (exclusively) on the basis of pyrolysis laws, Miller (2003) appreciated that if a pyrolysis law had to be established via measurement-based techniques for every combination of ingredients, the framework could not be considered predictive. Therefore, familiar with Zenin’s finding that a “universal” pyrolysis law held for a wide range of double-base propellant formulations, he investigated whether a single pyrolysis law could be employed for a wide range of nitramine-binder systems, and found that it could. However, that is only true to a point, and at a given P , the $\dot{m}$ values of pure HMX tend to be much higher than those of HMX–HTPB composites. Therefore, the study might have been better served by employing measured data specific to HMX–HTPB composites as the basis for specifying T_0 . Fortunately, as is discussed in Sections 3.5 and 3.6, the Hertz–Langmuir–Knudson-based representation of the condensed phase to gas-phase conversion process employed in the present CYCLOPS model does not fix the relationship between $\dot{m}$ and T^0 for all P , and $\dot{m}$ predictions at a given P proved to be relatively independent of the specification of T^0 .

the HR-CONP problems employed for the screening protocol. Therefore, no subsequent changes were made.

2.1.1.5 Simulation Temporal Length

The temporal durations of the simulations were chosen such that they exceeded by at least a factor of 2 the time at which the second of two major heat release events occurred (see Section 3.3). Though temperatures at these times did not reflect equilibrium values (to nine significant digits), we doubted there would be anything gained by getting closer to them.

2.2 TMM Screening Protocol

2.2.1 Screened Parameter Values

As in all previous TMM-based reduction efforts (but one) reported by our group (e.g., Kotlar 2010; McQuaid 2013; McQuaid and Chen 2014), parameters of the HR-CONP simulations that were compared were local maxima found in mass-specific and volumetric heat release rate ($\dot{q}_m^{max}$ and $\dot{q}_v^{max}$, respectively) versus time (t) histories, the times at which those maxima occurred (t_m^{max} and t_v^{max} , respectively), and the temperature at the final time step of the simulation (T_f).

The values of $\dot{q}_m(t)$ and $\dot{q}_v(t)$ were calculated per

$$\dot{q}_m(t) = R \left(T(t) * \sum_k \frac{dY_k(t)}{dt} / W_k + \frac{dT(t)}{dt} * \sum_k Y_k(t) / W_k \right) \quad (3a)$$

and

$$\dot{q}_v(t) = \rho_g(t) * \dot{q}_m(t), \quad (3b)$$

where Y_k is the k^{th} species' mass fraction, W_k is its molecular weight, and ρ_g is the gas mixture's density. Following the same reaction step order (minus those that had been permanently eliminated), the screening process was repeated for a given set of MADs if at least one reaction was permanently eliminated in the course of a complete pass through the mechanism. When no more reactions could be eliminated without exceeding any MAD (or 10 complete passes at a specified MAD level had been completed), the MADs were relaxed and the process repeated.

Table 1 summarizes important parameters of the screening protocols that were formulated and applied. The labeling of the protocols/sets (A, B, C, ...) reflects the chronological order in which they were performed. In set A, the protocol for setting the MADs for q_v^{max} , q_m^{max} , t_v^{max} , and t_m^{max} was similar to that employed for recent applications (i.e., ± 1.0 % for the first pass, then subsequently [and collectively]

relaxed in $\pm 1.0\%$ increments). Likewise, the tolerance for T_f was ± 1.0 K for the first pass, and it was subsequently relaxed (along with the MADs for the heat release rate parameters) in ± 1.0 K increments. The largest MADs allowed were $\pm 10\%$ and ± 10 K. When candidates with targeted sizes were not produced by that protocol, the protocols of the sets that followed were formulated in an attempt to address this issue, yet maintain a capacity to produce candidates that well mimicked the full mechanism near a deflagrating HMX–HTPB composite’s burning surface. The reasoning that led to the progression is discussed in more detail in Section 3.2.

2.2.2 Relative and Absolute Error Tolerances

The error test employed by DASPK includes parameters whose values are specified to reflect the maximum acceptable relative (RTOL) and absolute (ATOL) errors in state-variable values that can be tolerated. In SENKIN programs distributed by Sandia National Laboratories, DASSL family DAE solvers (to which DASPK belongs) are employed, and the default values are $\text{RTOL} = 1.0 \times 10^{-8}$ and $\text{ATOL} = 1.0 \times 10^{-20}$. We do not know the basis/rationale for these specifications, but assume they are “conservative”. (That is, solutions will not be meaningfully improved by specifying smaller values.) However, simulation runtimes are a function of them, and with the defaults specified, the (serial) runtimes of simulations based on the full mechanism exceeded 10 min. Facilitated by the parallelization of the program completed just prior to the start of the effort (Stone 2020), it would have been feasible to apply the TMM with the defaults specified. However, it would have been very computationally expensive, limited the number of candidates that could be produced, and involved extended turn-around times. Therefore, RTOL’s and ATOL’s values were systematically increased, the simulations rerun, and $T(t)$ and $\dot{q}_m(t)$ histories similar to those presented in this report compared to those produced with the defaults. Plots produced when RTOL was 1.0×10^{-5} and ATOL was 1.0×10^{-12} proved to be indistinguishable from those produced with the default values and the runtimes were reasonable. Therefore, the search was stopped and those values were specified.

2.2.3 Initial Reduction

Reviewing the results of simulations produced with the full mechanism, we observed that the Y_k of a large number of species were always 0.0 or never exceeded extremely small values. Considering it likely that the elimination of such species from the mechanism would not impact the values of the parameters that were compared by the screening protocol, we eliminated all species (and any reaction involving them) whose Y_k never exceeded ATOL (1.0×10^{-12}) in any of the solutions to set A’s screening protocol problems (see Section 2.2.2). This procedure was inspired by Lutz et al.’s (1988) observation that for DASSL family DAE

solvers, ATOL should be specified at a value well below the smallest significant state-variable value. Therefore, to the extent that specifying $\text{ATOL}=1.0 \times 10^{-12}$ was valid, the elimination of species whose Y_k never exceeded 1.0×10^{-12} was justified.

2.3 Mass Flux/Burning-Rate Calculations

To assess the validities of candidates for the intended application, they were employed with a CYCLOPS model to compute $r(P)$ and $\dot{m}(P)$ for pure HMX and a hypothetical homogeneous 80:20 HMX–HTPB mixture. Typically having “mean particle diameters” ranging from 100 to 500 μm , the spatial dimensions of the HMX particles in a HMX–HTPB composite are large compared to the width of the primary reaction zone at propulsion system operating pressures. Therefore, the composite is decidedly not well approximated as a homogenous mixture (e.g., Massa et al. 2007). Nevertheless, we thought simulations involving such a construct had the potential to be instructive.

The CYCLOPS framework is described in detail elsewhere (Miller and Anderson 2000). Briefly, it involves solving steady 1-D laminar premixed flame problems and finding values for $\dot{m}$ and T^0 such that two conditions are satisfied. One is the conservation of energy (flux) at the condensed-phase–gas-phase interface,

$$\left[\lambda_g \left(\frac{dT}{dx} \right) \right]^{+0} = \dot{m} \sum_k^K (Y_k^{-0} h_k^{+0} - Y_k^{-\infty} h_k^{-\infty}), \quad (4)$$

where, for a mechanism involving K species, λ_g is the thermal conductivity of the gas at the interface/surface ($x=0$), Y_k^{-0} are the mass fractions of the nascent products (k) of the condensed phase’s decomposition, h_k^{+0} are their enthalpies at T^0 , $Y_k^{-\infty}$ are the mass fractions of the condensed-phase’s ingredients, and $h_k^{-\infty}$ are their enthalpies at the condensed phase’s starting temperature ($T^{-\infty}$).

The second condition that has to be satisfied is the relationship between $\dot{m}$ and T^0 . For most of the calculations performed for pure HMX, the model employed a Hertz–Langmuir–Knudsen (HLK) relationship (Li et al. 1990; Miller 1997; Galwey and Brown 1999), viz.

$$\dot{m}_{\text{HMX}} = (W_{\text{HMX}}/2\pi RT^0)^{\frac{1}{2}} (X_{\text{HMX}}^{-0} A' \exp(-\Delta E/RT^0) - X_{\text{HMX}}^{+0} P), \quad (5)$$

where X_{HMX}^{-0} and X_{HMX}^{+0} are, respectively, the mole fractions of gas-phase HMX on the condensed- and gas-phase sides of the surface, P is the system’s pressure, A' is a (pre-exponential) constant for the function for computing HMX’s saturated vapor pressure (VP), and ΔE is the effective activation energy for sublimation.

For an initial set of calculations, A' (3.57×10^{18} dyn/cm²) and ΔE (40,600 cal/mol) were derived from a fit of the Clausius–Claperyon relation to measured values of HMX’s VP at temperatures between 370 and 500 K (Rosen and Dickinson 1969; Taylor and Crookes 1976). (As is discussed in Sections 3.4 and 3.5, T^0 were predicted to be considerably higher than 500 K, making the reliability of the predicted VP values uncertain.) In addition, while this report was being finalized, we found a very recent study by Morrison et al. (2021), who combined VPs they measured at temperatures near 300 K with those just mentioned and derived an A' (6.62×10^{16} dyn/cm²) and ΔE (36,200 cal/mol) that reasonably represented the aggregated data. VPs calculated on that basis proved to be a factor of 2 to 4 lower than those estimated by the initial set in the temperature range of interest (700–850 K). Therefore, the latter were employed for a limited set of calculations to assess the impact of the difference. A limited set of calculations were also performed based on Eq. 2 with constants established by Zenin and Finjakov (2009): $A = 1.1 \times 10^4$ g/cm²s and $B = 14,440$ cal/mol for $T^0 \leq 773$ K, and $A = 1.33 \times 10^7$ g/cm²s and $B = 25,000$ cal/mol for $T^0 \geq 773$ K.

Two different approaches were employed to establish the relationship between $\dot{m}$ and T^0 for the (hypothetical) homogeneous 80:20 HMX–HTPB formulation. In one, $\dot{m}_{HMX}$ was computed per Eq. 5 and the linear burning rate of HTPB ($r_{HTPB} = \dot{m}_{HTPB}/\rho_{HTPB}$) was set equal to the linear burning rate of HMX ($r_{HMX} = \dot{m}_{HMX}/\rho_{HMX}$). When r_{HTPB} equals r_{HMX} ,

$$\dot{m}_{HMX-HTPB} = (\rho_{HMX-HTPB}/\rho_{HMX})\dot{m}_{HMX}. \quad (6)$$

(To the extent that HMX–HTPB composite strands burn in cigarette fashion, the “effective” linear burning rates of HMX and HTPB are the same, but that result derives from dynamics that are multidimensional.) For the other relationship, the model employed Eq. 2 with constants established by Zenin (1998) for an 80:20 HMX–HTPB formulation: $A = 3.57 \times 10^3$ g/cm²s and $B = 12,750$ cal/mol.

The premixed flame simulations were performed with a model derived from a pre-commercial CHEMKIN III library of subroutines (Kee et al. 2002). Values of condensed-phase properties of HMX and HTPB employed for the calculations are shown in Table 2. Familiar with Zenin’s work and noting that his measurements were conducted with samples initially at 293 K, we employed that value for $T^{--\infty}$. (Writing this report, we realized that measurements were more commonly performed with samples initially at 298 K. However, from the standpoint of validating mechanisms, we believed the difference could be ignored.) We also note that the (commonly cited) density of room-temperature HMX is 1.91 g/cm³. However, as noted by Sinditskii et al. (2009), the density of the strands employed for the r_{HMX} measurements they aggregated were only 1.72–1.76 g/cm³.

Conversely, for the 80:20 HMX–HTPB composite, we calculated $\rho_{\text{HMX-HTPB}}$ via a mass-weighted average that employed 1.91 g/cm³ for ρ_{HMX} and 0.94 g/cm³ for ρ_{HTPB} . That approach yielded 1.54 g/cm³, which was near the 1.5 g/cm³ value Zenin (1998) reported for an 80:20 HMX–HTPB formulation. Therefore, that value was employed. Considering this ambiguity to be a potential source of confusion, we attempt to avoid it herein by presenting $\dot{m}$ values rather than r values.

Equation 4 was considered satisfied if its right- and left-hand sides were within 1.0% of one another. Equation 5 was considered satisfied if its right- and left-hand sides were within 5% of one another, or a change in T^0 less than 0.01 K was required to attain that level of agreement. Since in general our group considers an $\dot{m}$ prediction to be in good agreement with a measured $\dot{m}$ value if the two are within a factor of 2 of one another, these criteria were more than sufficient to exclude such considerations as a significant factor in a prediction not meeting that standard.

Table 2 Condensed-phase properties of HMX and HTPB used to calculate burning rates

Material	$\Delta H_f(298)$ (cal/g)	c_p (cal/mol-K)	ρ_c (g/cm ³)
HMX	61	69.4	1.74/1.91 ^a
HTPB	−30	186.2	0.94
80:20 HMX–HTPB	43	94.3	1.54

^aSee text for discussion.

3. Results

3.1 Screening Protocol HR-CONP Simulations: General Observations

There were six different HR-CONP simulations that were employed (in various combinations) for the screening protocols, with the primary difference between them being T_0 and P_0 . Those differences notwithstanding, their $T(t)$ and $\dot{q}_{m/v}(t)$ histories shared common characteristics, and to facilitate the discussion that follows, a brief overview of them is provided here.

Figure 1 presents $T(t)$ and $\dot{q}_m(t)$ histories obtained from a solution to one of the screening protocols’ problems. Two distinct heat release “events” occurred during the process. The first event produced a sharp increase in T that began to level out once T reached approximately 1200 K. Thereafter, dT/dt remained relatively modest until the second event occurred and the last of the stored chemical energy was released. Manifest as a “dark zone” in flames observed above strands of nitramines (and nitrate esters) burning in cigarette fashion at low (≤ 20 atm) pressures, the delay between events 1 and 2 causes visible light emission to stand

off a distance from the surface that is observable to the naked eye. Well-known and studied (e.g., Anderson et al. 2011a, 2011b), this phenomenon is understood to occur because nitric oxide (NO) produced by the decompositions of NO₂ and HONO is relatively slow to convert to nitrogen (N₂).

All the $T(t)$ and $\dot{q}_m(t)$ histories obtained from solutions to the HR-CONP problems used for the screening protocols exhibited this sequence of events, and the program decided to retain or eliminate a reaction based on the values of the (local) maxima in $\dot{q}_m(t)$ found for them ($\dot{q}_m^{max,1}$ and $\dot{q}_m^{max,2}$), and the t at which they occurred ($t_m^{max,1}$ and $t_m^{max,2}$). Not shown, $\dot{q}_v(t)$ histories, which were also a basis for the program's decision to retain or eliminate reactions, had analogous features that directly corresponded with the $\dot{q}_m(t)$ histories, viz. $\dot{q}_v^{max,1}$, $\dot{q}_v^{max,2}$, $t_v^{max,1}$, and $t_v^{max,2}$. Representing a slightly different measure of the heat release rate, $\dot{q}_v(t)$ histories could not in general be superimposed on their respective $\dot{q}_m(t)$ counterpart via simple linear scaling. Usually $\dot{q}_v^{max,1}/\dot{q}_v^{max,2}$ did not equal $\dot{q}_m^{max,1}/\dot{q}_m^{max,2}$, and $t_v^{max,1/2}$ and $t_m^{max,1/2}$ were often slightly different. Thus, computing and evaluating $\dot{q}_v(t)$ histories was not a completely redundant exercise. However, from the standpoint of candidate generation and validation, the differences between them and their corresponding $\dot{q}_m(t)$ history were not significant. Therefore, values of $\dot{q}_v^{max,1}$, $\dot{q}_v^{max,2}$, $t_v^{max,1}$, and $t_v^{max,2}$ derived from $\dot{q}_v(t)$ histories are not further discussed.

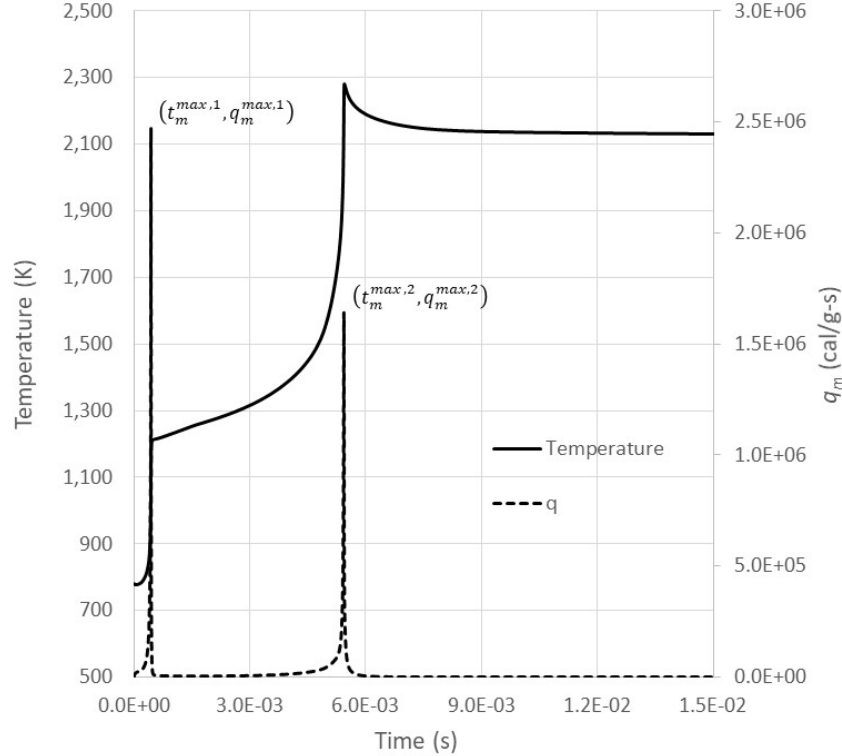


Fig. 1 Representative $T(t)$ and $\dot{q}_m(t)$ histories obtained from a solution to a screening protocol HR-CONP problem

3.2 Candidate Generation

As mentioned in the Introduction, we found that the TMM did not (and likely would not) produce skeletal mechanisms with 120 or fewer reactions and 120 or fewer species when the screening protocol specified MADs for $\dot{q}_m^{max}$, $\dot{q}_v^{max}$, t_m^{max} , t_v^{max} , and T_f that were similar to “standards” employed for previous reduction efforts (e.g., Chen and McQuaid 2020). Shown in Table 1, the standard MAD protocol was specified for the first set of orderings that was reduced (i.e., set A). Applied to the full (3825 reaction-1017 species) mechanism, the smallest mechanism produced had 156 reactions and 126 species, and thus was slightly larger than desired. (Its label [“A21”] refers to the set [A] that produced it and a unique initial ordering [21] of the reactions within that set.)

Given the dependence of candidate size on the initial ordering of the full mechanism’s reactions, one possibility for obtaining smaller candidates was simply to apply the standard protocol to more orderings. However, A21 was considerably smaller than the next smallest candidate produced by the other 39 orderings in set A. Therefore, we did not believe that approach would be fruitful. Instead, our first attempt to resolve this issue involved allowing the maximum MADs in $\dot{q}_m^{max}$, $\dot{q}_v^{max}$, t_m^{max} , and t_v^{max} for both events to relax to $\pm 20\%$ and the MADs in T_f to relax to ± 20 K. To assess this protocol’s potential to yield candidates with fewer than 120 reactions and fewer than 120 species, it was applied (in set B) to 10 different orderings of A21. For another submission (set C), the maximum MADs in $\dot{q}_m^{max}$, $\dot{q}_v^{max}$, t_m^{max} , and t_v^{max} for the second event (only) were allowed to relax to $\pm 20\%$ and the MADs in T_f allowed to relax to ± 20 K. The rationale for specifying different MADs for the parameters characterizing events 1 and 2 followed from a CYCLOPS-based study of the deflagration of NG by Chen et al. (2019). In that study, no correlation between the position of the 2nd $\dot{q}_{m/v}$ peak and the r predictions was observed (within the parameter space that was studied). Therefore, we assumed that larger differences between the parameters characterizing the second event in trial- and full-mechanism-based solutions would not make much difference in the conditions near the surface of a burning HMX–HTPB composite. Regardless, none of the candidates produced by these sets met the size objective.

Given those results, we reviewed the bounds of the parameter space to determine whether it could be reduced, and thereby hopefully reduce the size of the candidates. Consulting with Nusca (2018), we learned that 700 atm was the highest P for which he planned to simulate the composite’s deflagration. In addition, we performed CYCLOPS calculations to determine how the T^0 predictions compared to those derived on the basis of Miller’s nitramine-binder pyrolysis law (Miller 2003) and measured r for pure HMX (Sinditskii et al. 2009). As is discussed in

more detail in Sections 3.4 and 3.5, at a given P , the CYCLOPS-based T^0 predictions based on an HLK relationship were lower than those based on the pyrolysis law, and the range of T^0 was reduced as well. Therefore, we specified T^0 values that were more in line with the HLK-based predictions for subsequent submissions.

At that point, it also was clear that a significant number of species and reactions could (and should) be eliminated based on the criteria discussed in Section 2.2.3. That is, if in every simulation employed for the screening protocol a species' mass fraction never exceeded ATOL's value, it and any reaction involving it was eliminated. In all, 618 reactions and 192 species were eliminated on that basis, leaving a mechanism with 3199 reactions and 825 species. To check the impact the eliminations had on the solutions to the screening protocols' problems, $T(t)$ and $\dot{q}_m(t)$ histories produced with this mechanism were visually compared to those produced with the full mechanism, and they proved to be indistinguishable at the scales at which they were plotted (e.g., Fig. 1). Therefore, the 3199 reaction-825 species mechanism was employed as the starting point for further reductions (i.e., sets D, F, and G). This mechanism is referred to hereafter as SM(3199R-825S).

Based on the candidates produced by set C, we thought the program had the potential to produce candidates with acceptable sizes for the reduced parameter space using a MAD protocol similar to the one employed for set C. However, the smallest candidates produced by set D had sizes similar to those produced by set C. Therefore, one of those candidates (D02) was further reduced (via set E) by further relaxing the MADs for the 2nd $\dot{q}_{m/v}$ peak and T_f . However, the numbers of reactions and species eliminated were small.

Although set E did not produce any candidates with as few as 120 reactions, we specified the protocols employed for sets F and G to reach maximum MADs that were similar. Again, because candidate sizes are dependent on the initial ordering of the reactions and candidates approaching targeted sizes were produced by set E, we thought there was a chance that such candidates had the potential to be produced by them. None were.

Not making progress, and uncomfortable with relaxing MADs any further, we decided to evaluate candidates produced to that point. Finding that CYCLOPS-based $\dot{m}(P)$ predictions for pure HMX were in reasonable agreement with measured values, and confirming that mechanisms in the size range obtained could be employed by the 2-D laminate CFD model, we did not submit any more reductions.

3.3 Comparison of Results for Screening Protocol HR-CONP Simulations

As discussed in prior reports (e.g., Chen and McQuaid 2016), the screening protocol can produce “false positives” (i.e., solutions with $T(t)$ and $\dot{q}_{m/v}(t)$ histories for which no MADs are exceeded, but they do not agree well with histories produced with the full mechanism when viewed in their entirety). Therefore, the $T(t)$ and $\dot{q}_m(t)$ histories obtained from the solutions to the screening protocol problems produced by all the candidates listed in Table 2 were plotted to check for that possibility. None were found.

The comparisons were also a basis for selecting the candidate to employ for the 2-D laminate CFD model. Figures 2–4 compare the histories produced with the candidate that was ultimately recommended for use in the model (i.e., E10d) to those produced with the full mechanism. Overall, we were satisfied with the agreement.

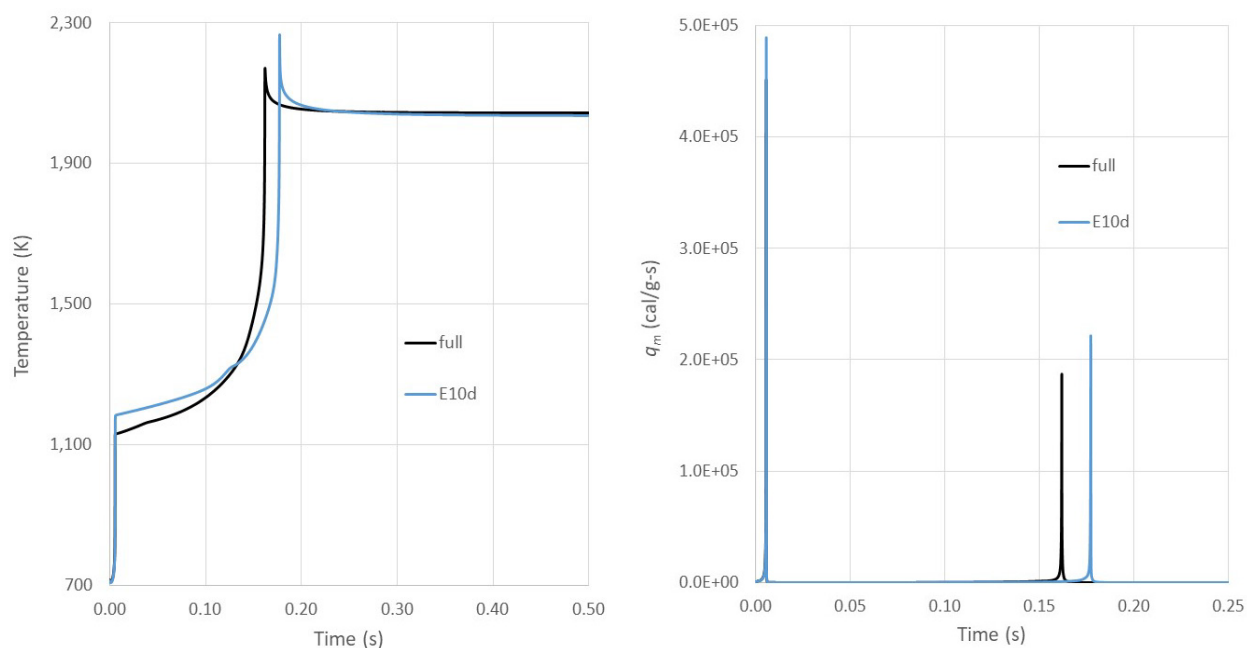


Fig. 2 Comparisons of $T(t)$ and $\dot{q}_m(t)$ histories obtained from solutions to set E’s 10 atm screening protocol problem: E10d vs. the full mechanism. Note the difference in the figures’ timescales.

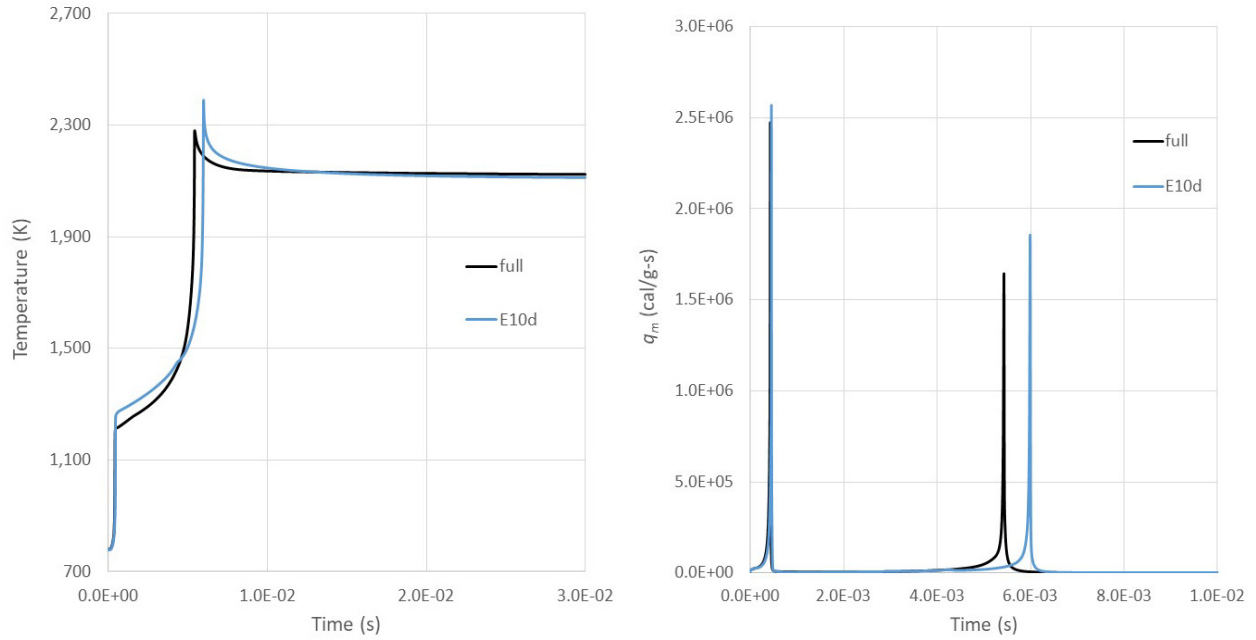


Fig. 3 Comparison of $T(t)$ and $\dot{q}_m(t)$ histories obtained from solutions to set E's 100 atm screening protocol problem: E10d vs. the full mechanism. Note the difference in the figures' timescales.

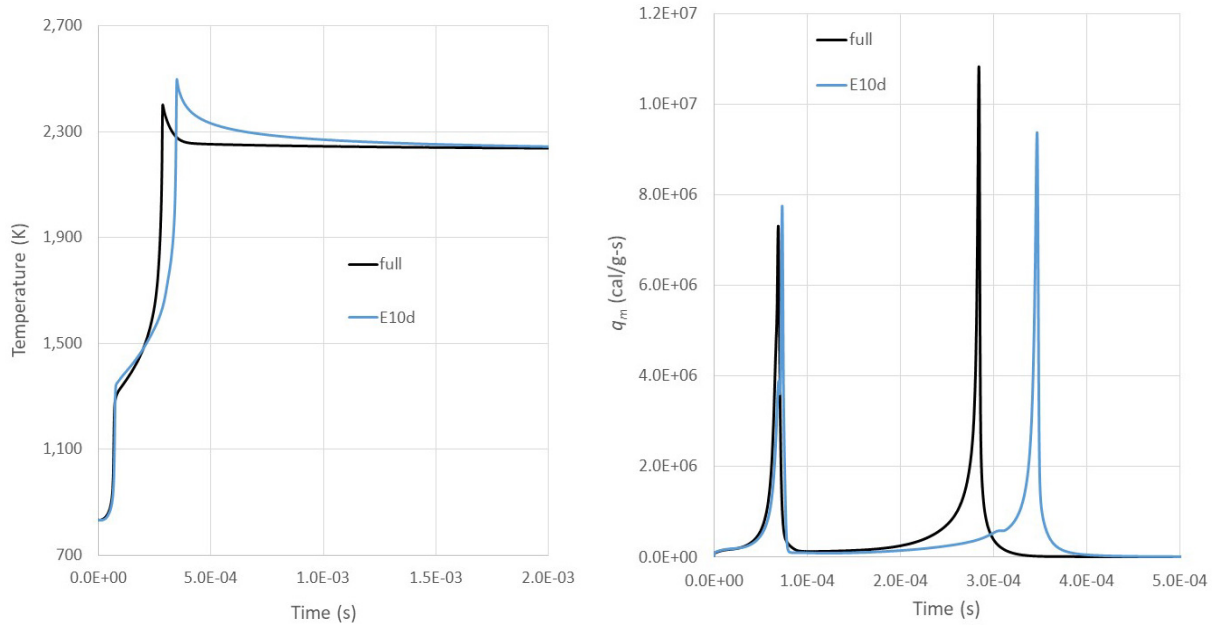


Fig. 4 Comparison of $T(t)$ and $\dot{q}_m(t)$ histories obtained from solutions to set E's 700 atm screening protocol problem: E10d vs. the full mechanism. Note the difference in the figures' timescales.

3.4 CYCLOPS-Based Predictions for Pure HMX Deflagration: SM(3199R-825S)

Prior to presenting the $\dot{m}_{HMX}$ predictions produced with E10d and some of the other candidates, it is instructive to consider CYCLOPS-based predictions for the deflagration of pure HMX produced with SM(3199R-825S). Compared in Fig. 5 to $\dot{m}_{HMX}$ values derived from measured r data aggregated by Sinditskii et al. (2009) (assuming ρ_{HMX} was invariant over the given P range), CYCLOPS-based $\dot{m}_{HMX}$ predictions obtained with the HLK-based representation for the condensed-phase-to-gas-phase conversion process (i.e., Eq. 5 with $A' = 3.57 \times 10^{18} \text{ g/cm}^2\text{s}$ and $\Delta E = 40,600 \text{ cal/mol}$) were found to be in good agreement with the measured values over the entire pressure range of interest.

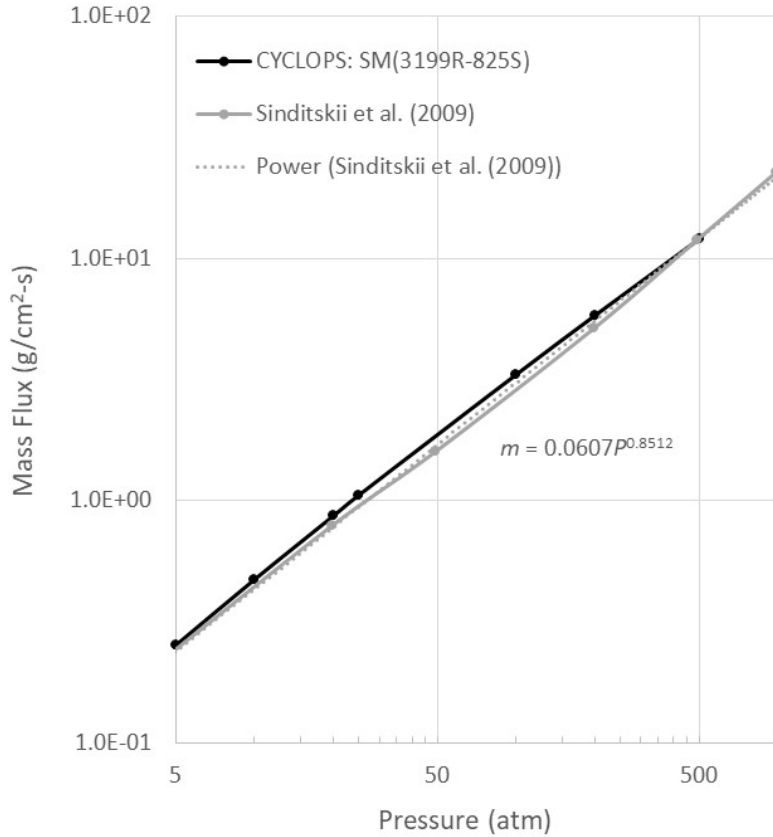


Fig. 5 Comparison of measured and SM(3199R-825S)-based $\dot{m}_{HMX}(P)$ values

As observed by Sinditskii et al. (2009), a Vieille's law fit to the measured data indicates n increases slightly with increasing P . The CYCLOPS-based calculations predicted n decreases slightly with increasing P . Nonetheless, we considered Fig. 5 persuasive evidence for the validity of the full HMX–HTPB mechanism for modeling the combustion of pure HMX.

We note that when (as in the current study) the interface between the condensed and gas phases is modeled as a plane, we expect CYCLOPS-based $\dot{m}_{HMX}$ predictions to be slightly lower than measured values, because the surface area of a burning energetic material is likely to be larger than that approximation (McQuaid and Chen 2014). Therefore, we would normally be inclined to downplay (somewhat) the close agreement obtained. However, surface roughness is also an issue in deriving temperature measurements from embedded thermocouples, and Zenin and Finjakov, who observed the surfaces of quenched HMX samples via a microscope, concluded the character of the deflagration of those samples was close to 1-D over the entire burning surface. Coupled with the results shown in Fig. 5, that finding lends additional credence to SM(3199R-825S)’s capacity to represent the gas-phase combustion chemistry associated with HMX’s deflagration.

We also considered the comparison evidence for the validity of the HLK relationship employed to model the condensed-phase-to-gas-phase conversion process. Predicating that the process is simply sublimation, it belies the need to include a complementary condensed-phase reaction mechanism (at least in this P range). Employing a pyrolysis law to simulate the process, Prasad et al.’s eigenvalue method predicted that the percent decomposition of the liquid phase was less than or equal to 0.2% for P greater than or equal to 50 atm, implying (like the CYCLOPS model) that the condensed-phase-to-gas-phase conversion process is simply a phase change.

Employing the HLK relationship, the CYCLOPS model also produced predictions for T^0 as a function of P , which, coupled with the $\dot{m}_{HMX}$ predictions, offer an alternative basis for establishing a pyrolysis law. Displayed in Fig. 6, the data was well fit with $A = 1.439 \times 10^{10} \text{ g/cm}^2\text{s}$ and $B = 34,390 \text{ cal/mol}$.

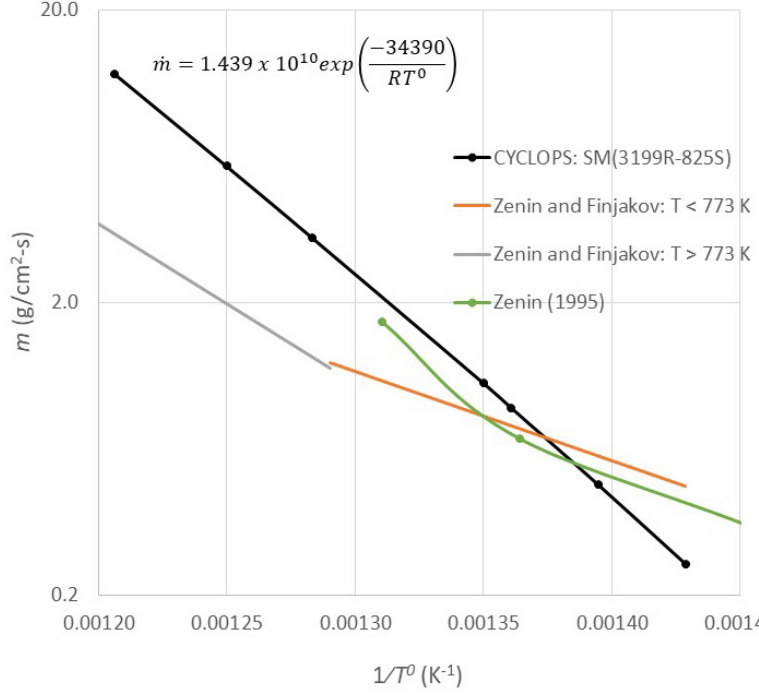


Fig. 6 $\dot{m}_{HMX} - T^0$ relationships

Shown for comparison are the relationships predicted by the pyrolysis laws for pure HMX published by Zenin and Finjakov (2009). Those laws suggest that the T^0 for $P > 20$ atm are much higher than those predicted by the CYCLOPS model. As discussed in Section 3.5, the $\dot{m}_{HMX}$ predictions produced at a given P with E10d proved to be relatively insensitive to the specification of T^0 , which calls into question the use of such a representation for modeling the condensed-phase-to-gas-phase conversion process associated the HMX's deflagration. Beyond that, we note that Zenin and Finjakov's pyrolysis law indicates that to produce an order of magnitude increase in $\dot{m}_{HMX}$ for $P > 10$ atm, T^0 has to rise over 100 K. Given that the VP of HMX increases more than 4 orders of magnitude between 373 and 473 K (Morrison et al. 2021), we question whether a 100 K increase in T^0 would actually be needed to effect an order of magnitude change in $\dot{m}_{HMX}$. It has long been appreciated that “the rate of evaporation from the free surface of a superheated liquid is extremely great, and superheating of it is practically impossible” (Zeldovich 1942), and it is hard to imagine that the T^0 values predicted by Zenin and Finjakov's pyrolysis laws do not correspond to superheated values.

We also note that in Prasad et al.'s model, the analog to T^0 in the CYCLOPS model was specified/fixed based on measured data published by Zenin (1995). Shown in Fig. 6, the T^0 measured at the highest P (and $\dot{m}$) considered in that study (70 atm) had a much lower value than would be predicted on the basis of the pyrolysis law

Zenin and Finjakov published in 2009. (We verified that the pyrolysis laws reflected the measured values from which they were derived.)

Interestingly, the $(\dot{m}_{HMX}, T^0)$ values reported in Zenin's 1995 paper for pure HMX burning at 20 atm (0.4 g/cm²s, 733 K) and 70 atm (1.0 g/cm²s, 763 K) agree well with the CYCLOPS-based predictions. Zenin and Finjakov (2009) state, "methods of surface temperature measurement have been developed and improved for a long time", but the 1995 paper is not referenced and it is not clear to us why they considered the values they published in 2009 more reliable. Based on the considerations discussed in the preceding paragraph, we believe the values in the 1995 paper are more reasonable.

Finally, we compared the SM(3199R-825S)-CYCLOPS-based predictions for $T(x)$ and $\dot{q}_v(x)$ profiles for pure HMX burning at 100 atm to profiles for pure HMX burning at 98.7 atm (10 MPa) that were published by Zenin and Finjakov (2009). Shown in Fig. 7, the temperature at the surface was very similar in both cases, but the predicted T values rose much more quickly and reached a much higher level: 3300 K versus 2700 K. The $\dot{q}_v(x)$ profiles were also significantly different. Overlooking the differences in the magnitudes, which may be due to different bases for computing $\dot{q}_v$, we observed that the CYCLOPS model predicted that the process proceeds via an endothermic event followed by two distinct exothermic events occurring in rapid succession much closer to the surface. Observed in the results presented by Hatch (1987), the sequence of events revealed by the simulations indicates diffusion played an important role in the dynamics.

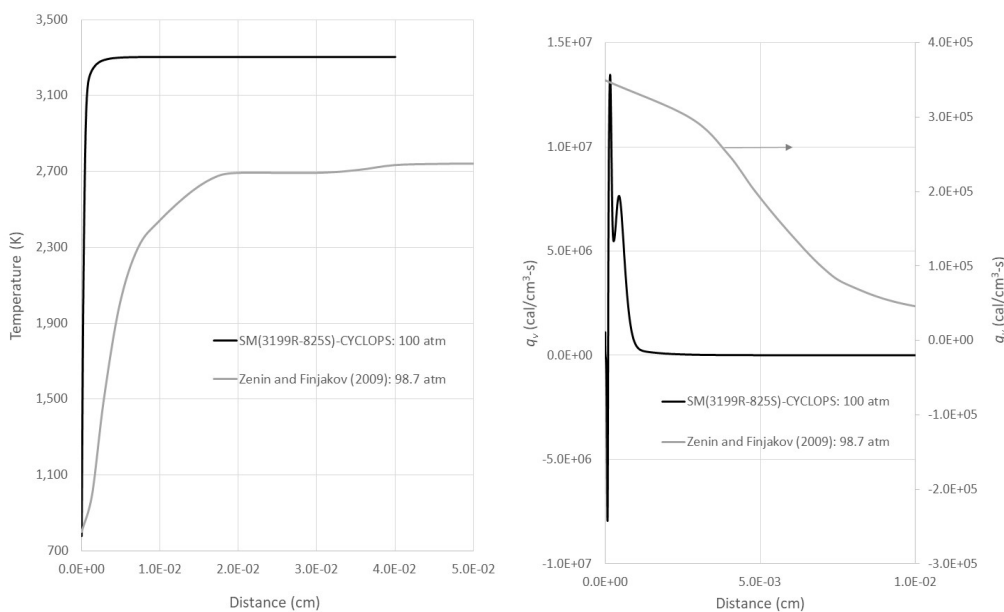


Fig. 7 Comparison of the $T(x)$ and $\dot{q}_v(x)$ profiles for pure HMX burning at approximately 100 atm: SM(3199R-825S)-based predictions vs. measured values

While we do not consider ourselves qualified to judge Zenin’s methods and results, given that the adiabatic flame temperature of HMX is generally accepted to be approximately 3200 K (Beckstead and McCarty 1982), and the final temperature reached in the CYCLOPS simulation (3300 K) is the value derived on the basis of our thermodynamic data base, it would appear that the process measured by Zenin and Finjakov was fairly far from adiabatic.

3.5 CYCLOPS-Based Predictions for Pure HMX: E10d

Figure 8 compares the $\dot{m}_{HMX}$ predictions based on mechanisms E10a-d to those based on SM(3199R-825S). E10a was the smallest candidate produced by set E. E10d, which had two more reactions, was created by the pass immediately preceding the pass that produced E10a. As the figure shows, the addition of the two reactions produced nearly a factor of 2 increase in the $\dot{m}_{HMX}$ predictions.

Curious about the difference, we built E10b and E10c by adding to E10a one of the two additional reactions in E10d. Specifically,



was included in E10b and



was included in E10c. As shown in Fig. 8, the $\dot{m}_{HMX}(P)$ predictions produced with E10b were nearly identical to those produced with E10a, while the $\dot{m}_{HMX}(P)$ predictions produced with E10c were similar to those produced by E10d. While this could be taken to suggest that the difference was caused primarily by R2, the deflagration of pure HMX certainly has negligible potential to produce $\text{CH}_2\text{CHCHCH}_2$ or $\text{CH}_2\text{CHCHCH}\cdot$, and therefore R2 has negligible potential to impact $\dot{m}_{HMX}$. Rather, we considered it likely that the observed differences were an artifact of the numerics. In particular, the finite-difference approximation employed to calculate $(dT/dx)^{+0}$ has been observed to be very sensitive to small changes in T when grid spacings near the surface are extremely small.

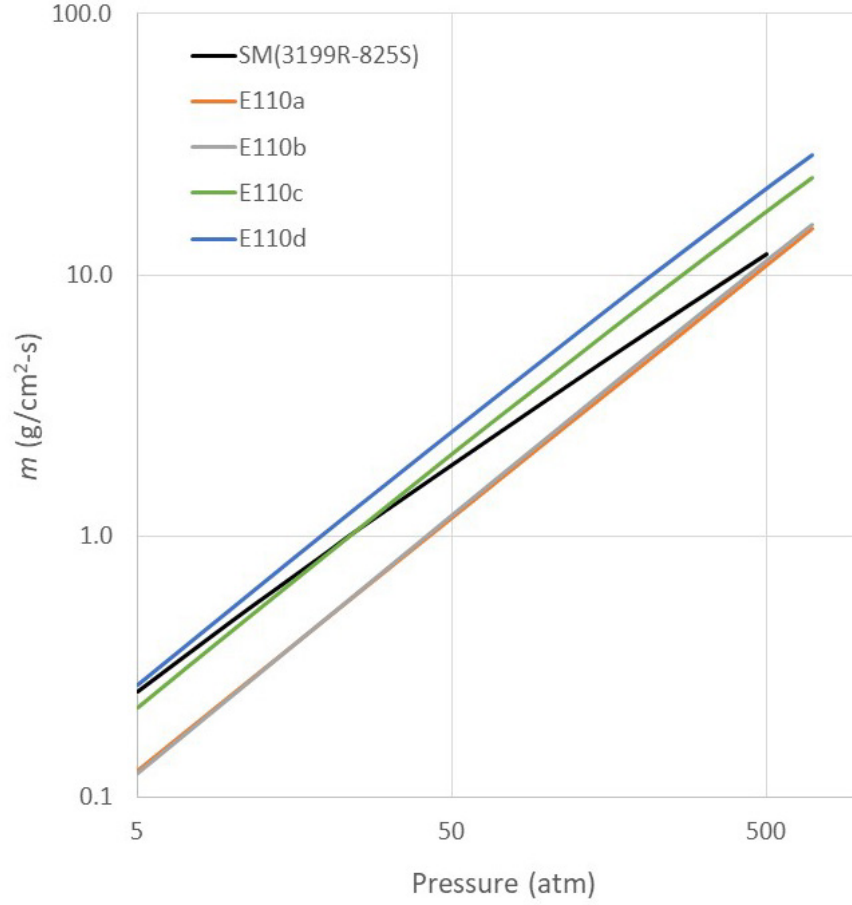


Fig. 8 Comparison of CYCLOPS-based $\dot{m}_{HMX}$ predictions produced with SM(3199R-825S) and E10a-d

The source of the differences could (perhaps) have been verified by specifying more exacting convergence criteria and/or performing deeper analyses. However, we did not believe such an effort, which could have been considerable, was warranted. The $\dot{m}_{HMX}(P)$ predictions produced with E10d were within a factor of 2 of their respective measured value, and that is a standard of agreement with which we are generally satisfied. Given all the assumptions upon which the CYCLOPS framework is based and the nonlinear nature of the dynamics, we do not think it realistic to expect better agreement.

That perspective also applied to ranking candidates' capacities to mimic the full mechanism within the parameter space of interest. Because the CYCLOPS framework is less complex, there is no guarantee that achieving higher levels of agreement between CYCLOPS-based $\dot{m}_{HMX}$ predictions and measured values will translate into proportional improvements in the predictions produced by a multidimensional CFD model of a temporally transient process. As such, from the standpoint of selecting a candidate for the application, we believed there was little

to be gained by resolving the issue. Therefore, we stopped the candidate evaluation process, selected E10d for the application, and transitioned it for use in the 2-D laminate CFD model. All the inputs needed to construct E10d are provided in an addendum to this report (Chen et al. 2021).

Given the difference between the $\dot{m}_{HMX} - T^0$ relationships predicted by Zenin and Finjakov's pyrolysis law(s), our original HLK formula, and the HLK formula derived on the basis of the VP data recently published by Morrison et al. (2021), we were curious as to how the CYCLOPS-based $\dot{m}_{HMX}$ predictions would vary as a function of these relationships. Employing E10d as the basis for the predictions, we found (much to our surprise) that the $\dot{m}_{HMX}(P)$ plots produced with each relationship were almost identical over the entire pressure range of interest (Fig. 9). Rather, it was the T^0 predictions that were significantly impacted (Fig. 10).

Although we had observed $\dot{m}_{HMX}(P)$ predictions to be relatively independent of the value of T^0 in the case of AP (McQuaid et al. 2014), the independence of $\dot{m}_{HMX}(P)$ with respect to T^0 indicated by Figs. 9 and 10 took us aback. The results obtained at 700 atm were particularly eye-opening; nearly identical $\dot{m}_{HMX}$ predictions were produced when T^0 was 850 K and when it was 1220 K. Given the exponential dependence of $\dot{m}_{HMX}$ with respect to $1/T^0$ implied by Eq. 2, the result is completely counterintuitive. Indeed, the results presented in Figs. 9 and 10 call into question the use of Eq. 2 (or any other formula dependent solely on T^0) as a basis for calculating the mass flux of the condensed-phase-to-gas-phase conversion process.

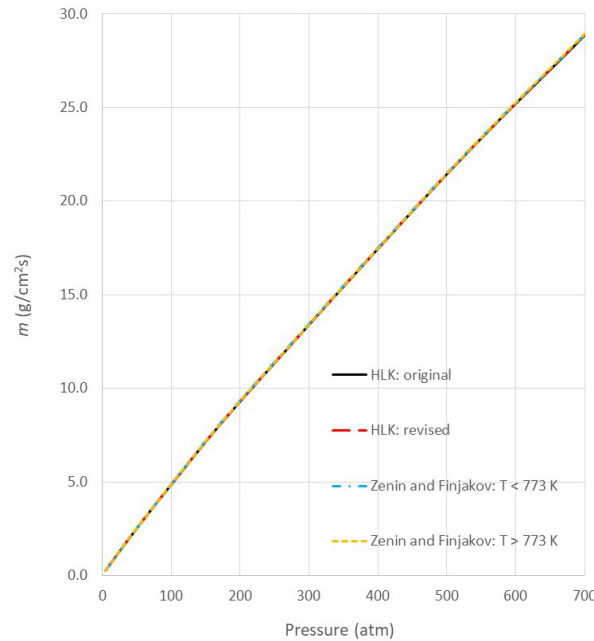


Fig. 9 Comparison of E10d-based $\dot{m}_{HMX}$ predictions produced with different $\dot{m}_{HMX} - T^0$ relationships

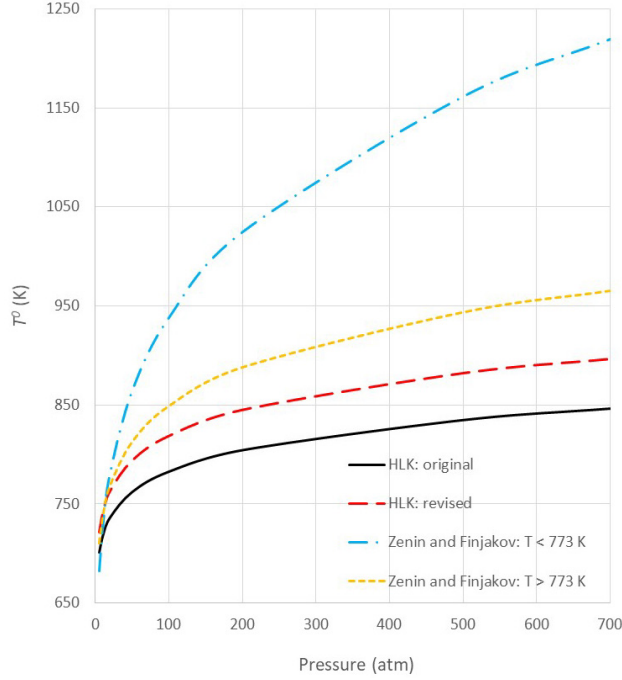


Fig. 10 Comparison of E10d-based T^0 predictions produced with different $\dot{m}_{HMX} - T^0$ relationships

To explore this matter somewhat further, we plotted $T(x)$ and $\dot{q}_m(x)$ results produced with the four condensed-phase-to-gas-phase conversion relationships upon which the results presented in Figs. 9 and 10 were based. For these comparisons, $\dot{q}_m$ was computed per

$$\dot{q}_m = \sum_{k=1}^K h_k \dot{\omega}_k W_k / \rho_g, \quad (7)$$

where h_k is the k^{th} species' mass-specific enthalpy and $\dot{\omega}_k$ is its molar production rate.

Figure 11 shows the results obtained from solutions for the 100-atm case based on the relationships that yielded the T^0 predictions that differed the most (i.e., the original HLK relationship and Zenin and Finjakov's pyrolysis law for $T^0 < 773$ K). At 100 atm, the T^0 predicted by these two relationships differed by more than 150 K: 783 K versus 939 K. (We appreciate that Zenin and Finjakov did not intend for their law to be used for $T^0 > 773$ K. We employed it merely to demonstrate our point.) Nonetheless, the plots are very similar at the scales presented in the figure.

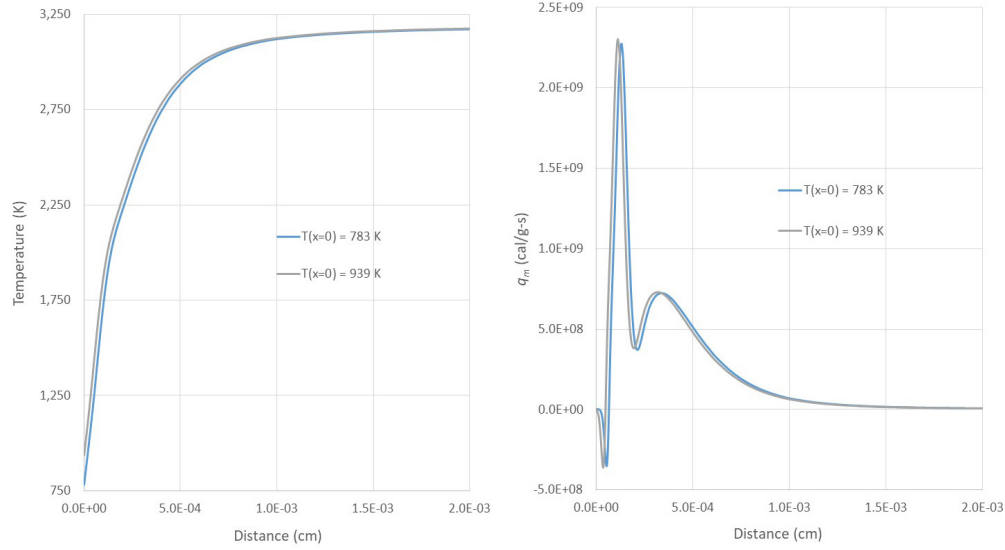


Fig. 11 Comparison of $T(x)$ and $\dot{q}_m(x)$ predictions obtained from E10d-based simulations for pure HMX burning at 100 atm: $T^0 = 783$ K vs. $T^0 = 939$ K

As might be expected, the first exothermic event occurred closer to the surface when T^0 was 939 K, and the temperature rose more quickly. However, the higher heat feedback to the surface those dynamics created did not result in a higher $\dot{m}_{HMX}$ (presumably) because it was needed simply to sustain the production of the nascent product (i.e., HMX gas) at the higher T^0 .

These results have implications for the formulation of a representation for calculating $\dot{m}_{HMX}$ from the surface of an HMX crystal in an HMX-HTPB composite. Observing the monotonic change in $\dot{m}_{HMX}$ with P and the monotonic relationship between $\dot{m}_{HMX}$ and T^0 indicated by the pyrolysis laws derived by Miller and Zenin, one might be led to believe that T^0 at a given P is well determined. Our results indicate that need not be the case. Massa et al. (2007) presented and discussed a pyrolysis law with the form

$$\dot{m} = AP^n \exp\left(-\frac{B}{RT^0}\right). \quad (8)$$

However, they set n equal to 0 (without explanation). We suggest that the $\dot{m}_{HMX}$ at a (local) grid point in a multidimensional CFD model can be assumed to depend only on the P at that grid point; T^0 would appear to be irrelevant (within bounds).

E10d-based results such as those shown in Fig. 11 also raised the question as to how they compared to those produced with SM(3199R-825S). Results obtained for pure HMX burning at 100 atm are shown in Fig. 12. Qualitatively, the $\dot{q}_m(x)$ plots were similar; both have an endothermic event near the surface followed by two distinct exothermic events. The magnitudes of the endotherm and the first exotherm

produced with E10d were greater than those produced with SM(3199R-825S), and they were closer to the surface. Despite these differences, the similarity of the sequences suggests the same subsets of reactions are important in both. The sequence produced by E10d led to the temperature rising faster closer to the surface. This result is reflected in the higher $\dot{m}_{HMX}$ predicted when E10d was the basis for the simulation.

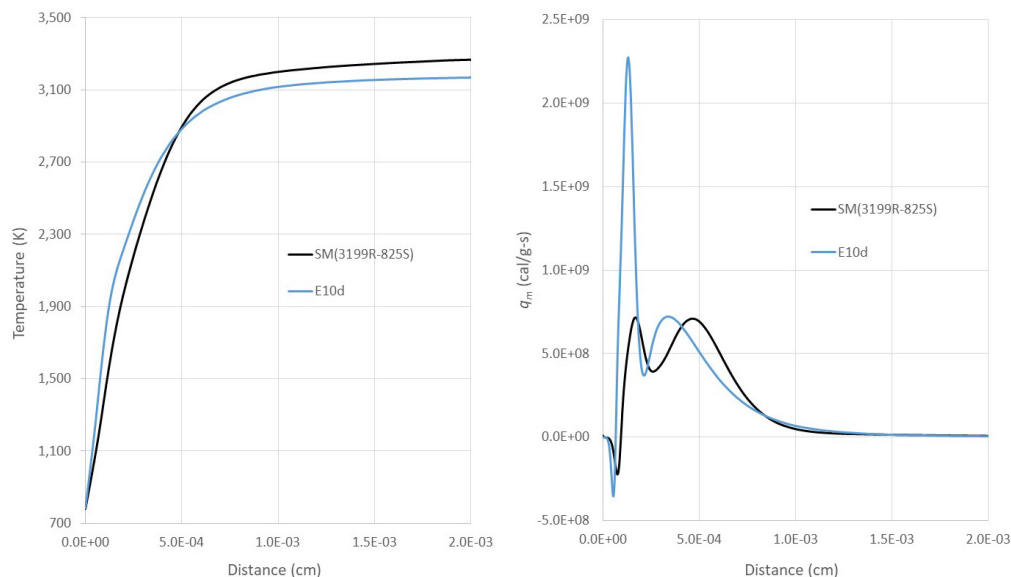


Fig. 12 Comparison of $T(x)$ and $\dot{q}_m(x)$ predictions obtained from SM(3199R-825S) and E10d-based simulations for pure HMX burning at 100 atm

3.6 CYCLOPS-Based Predictions for a Homogeneous HMX-HTPB Composite

As mentioned in the Introduction, the effort summarized herein was undertaken because we thought a study of HMX–HTPB composite deflagration would supplement our knowledge of crystal cracking and crevice formation that appear to underlie the change in the pressure dependence of the burning rate of AP–HTPB composites. The CYCLOPS framework has very limited capacity to provide insight into such mechanisms. (It can be formulated to study the impact of increased surface area due to surface roughness and/or spall, but it cannot model their generation [McQuaid and Chen 2016].) Nonetheless, we thought its predictions for a hypothetical homogeneous mixture might be instructive.

Figure 13 compares CYCLOPS-based $\dot{m}_{HMX-HTPB}(P)$ predictions for 80:20 HMX–HTPB to values measured by others. (The predicted results in the figure were obtained with Eqs. 5 and 6 employed to represent the mass flux of the condensed-phase-to-gas-phase conversion process.) Measured values for pure HMX are also shown. We observed that, at a given P , the predicted $\dot{m}_{HMX-HTPB}$

values were about an order of magnitude lower than the respective measured value. As mentioned in Section 3.4, we generally expect predicted values to be (somewhat) lower than measured values, but the differences observed caused some initial concern. That passed, however, when the $\dot{m}_{\text{HMX-HTPB}}$ predictions produced with E10d proved to be very similar to those produced with SM(3199R-825S).

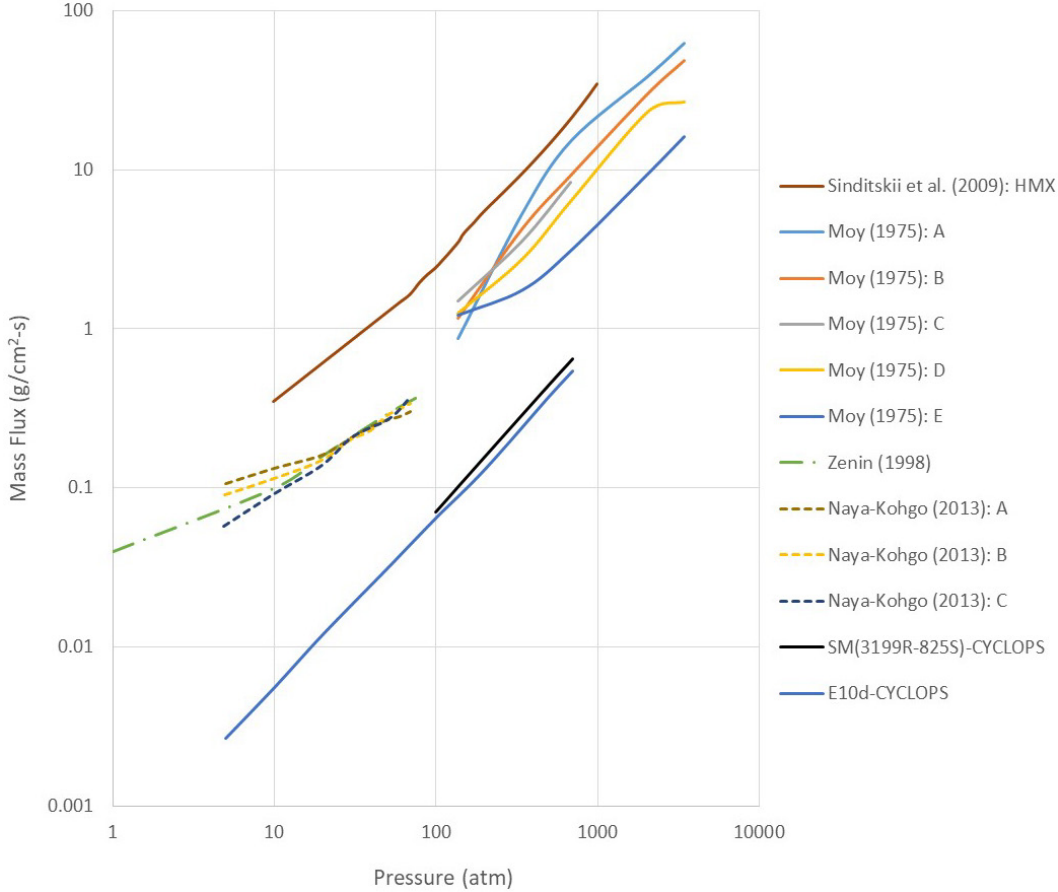


Fig. 13 Comparison of measured and CYCLOPS-based $\dot{m}(P)$ predictions for 80:20 HMX-
HTPB composites

Curious as to whether $\dot{m}_{\text{HMX-HTPB}}$ predictions would demonstrate the same insensitivity to T^0 that was observed for pure HMX, we employed Zenin’s pyrolysis law for 80:20 HMX-
HTPB composites to calculate the mass flux of the condensed-phase-to-gas-phase conversion process for a separate set of simulations (see Section 2.3). Perceiving that the answer would not inform the 2-D laminate CFD modeling effort, where different formulae can be employed to calculate the regression rates for the two ingredients, we limited the effort to a single submission and only obtained converged solutions at two pressures: 5 and 100 atm. As was found for pure HMX, very similar $\dot{m}_{\text{HMX-HTPB}}$ predictions were obtained at significantly different T^0 in these two cases. At 5 atm, the $\dot{m}_{\text{HMX-HTPB}}$ prediction

based on the pyrolysis law was $2.68 \times 10^{-3} \text{ g/cm}^2\text{s}$ versus the $2.66 \times 10^{-3} \text{ g/cm}^2\text{s}$ predicted with Eqs 5 and 6, while the T^0 predictions were 639 and 677 K, respectively. At 100 atm, the $\dot{m}_{\text{HMX-HTPB}}$ prediction based on the pyrolysis law was $6.51 \times 10^{-2} \text{ g/cm}^2\text{s}$ versus the $6.46 \times 10^{-3} \text{ g/cm}^2\text{s}$ predicted with Eqs 5 and 6, while the T^0 predictions were 706 and 752 K, respectively.

We also compared $T(x)$ and $\dot{q}_m(x)$ plots produced with E10d and SM(3199R-825S). Figure 14 shows the results produced at 100 atm. We note that, compared to pure HMX burning at the same pressure, the length scale of the flame is over an order of magnitude longer (compare to Fig. 12). In addition, an endothermic event did not precede the two main exothermic events.

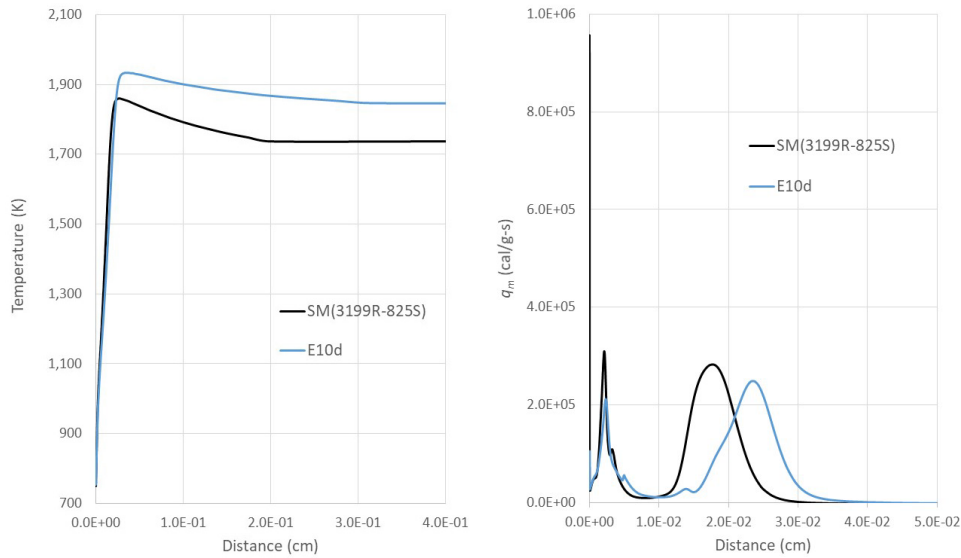


Fig. 14 Comparisons of CYCLOPS-based $T(x)$ and $\dot{q}_m(x)$ predictions for an 80:20 HMX-HTPB composite burning at 100 atm: SM(3199R-825S) vs. E10d. Note the difference in the length scales.

As was expected on the basis of the similarity of the $\dot{m}_{\text{HMX-HTPB}}$ predictions produced with the two mechanisms, the $T(x)$ profile produced with E10d reasonably resembled that produced with SM(3199R-825S) near the surface. The temperature transient produced with E10d subsequently led to a maximum temperature that was approximately 70 K higher than the one produced with SM(3199R-825S). In both cases, the temperature then declined from its maximum, and the final temperature difference was approximately 110 K. Given that the overall temperature rise was greater than 1000 K, we considered the difference acceptable. Likewise, the $\dot{q}_m(x)$ plots indicated that the reactions and species most responsible for heat release events produced with SM(3199R-825S) were in E10d.

4. Summary and Conclusion

The TMM was employed to reduce a large (3825 reaction-1017 species) finite-rate chemical kinetics mechanism for modeling the gas-phase combustion associated with the deflagration of HMX–HTPB composites. Seeking skeletal mechanisms for use in a time-accurate 2-D laminate CFD model of the phenomenon, the screening protocol was based on comparing results obtained from solutions to HR-CONP problems. The candidate that was selected for use in the 2-D laminate CFD model comprised 135 reactions and 117 species. Called E10d, its selection was based in part on $\dot{m}(P)$ predictions for pure HMX it produced in conjunction with a CYCLOPS model. Calculated values were found to be less than 50% greater than measured values at pressures from 5 to 700 atm.

In the course of evaluating E10d, it was observed that $\dot{m}(P)$ predictions at a given pressure were effectively independent of the temperature of the interface between the condensed and gas phases. That result calls into question the use of representations for calculating the mass flux of the condensed-phase-to-gas-phase conversion process that are formulated solely in terms of the surface temperature.

The CYCLOPS model was also employed to predict $\dot{m}(P)$ values for a hypothetical homogeneous HMX–HTPB mixture. The predictions were significantly lower than values reported for heterogeneous HMX–HTPB composites. But that result was expected because the condensed-phase-to-gas-phase conversion processes of HMX and HTPB are different, making the effective surface area of a deflagrating composite greater than the simple plane employed to represent it in the model. In addition, $\dot{m}(P)$ predictions produced with E10d and a very large subset of the full mechanism were in reasonable agreement, suggesting E10d will reasonably mimic the full mechanism within the parameter space of interest. All the inputs needed to construct E10d are provided in an addendum to this report (Chen et al. 2021).

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List of Symbols, Abbreviations, and Acronyms

A	Vieille's law (Eq. 1) or pyrolysis law (Eq. 2) preexponential constant
A'	HLK (Eq. 5) representation constant
B	pyrolysis law (Eq. 1) constant
AP	ammonium perchlorate
ATOL	absolute tolerance parameter
CFD	computational fluid dynamics
CONP	closed adiabatic system at constant pressure
c_p	heat capacity at constant pressure
CYCLOPS	1-D steady laminar deflagration model
DAE	differential-algebraic equation (system)
ΔE	HLK representation constant
$\Delta H_f(298)$	enthalpy of formation at 298 K
h_k	mass-specific enthalpy of the k^{th} species
HLK	Hertz–Langmuir–Knudsen
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocane
HONO	nitrous acid
HR	homogeneous reactor
HTPB	hydroxyl-terminated polybutadiene
k	species index
λ_g	thermal conductivity
$\dot{m}$	mass flux
MAD	maximum acceptable deviation
n	pressure exponent for a Vieille's law representation of the burning rate
N ₂	nitrogen
NG	nitroglycerine
NO	nitric oxide

NO_2	nitrogen dioxide
P	pressure
$\dot{q}_m$	mass-specific heat release rate
$\dot{q}_v$	volumetric heat release rate
ρ_c	density of the condensed phase
ρ_g	density of the gas phase
r	burning/regression rate
R	universal gas constant
RFNA	red fuming nitric acid
RDX	1,3,5-trinitro-1,3,5-triazinane
RTOL	relative tolerance parameter
T	temperature
T^0	temperature at $x = 0$ in the CYCLOPS model
T_0	temperature at $t = 0$ in the HR-CONP model
t	time
TMM	trial mechanism method
VP	(saturated) vapor pressure
W_k	molecular weight of the k^{th} species
$\dot{\omega}_k$	molar production rate of the k^{th} species
x	spatial dimension
X_k	mole fraction of the k^{th} species
Y_k	mass fraction of the k^{th} species

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