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Computationally Based Predictions for the Burning Rates and Flame Structures of Nitroglycerin Doped with Various Small Molecules

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14. ABSTRACT A CYCLOPS-based model was employed to simulate the steady laminar deflagration of liquid nitroglycerin [NG(l)] and mixtures of it with various small molecules, including hydrazoic acid, hydrazine, ammonia, isocyanic acid, formaldehyde, and urea. Employing a detailed, finite-rate chemical kinetics mechanism that included elementary reactions for decomposing the parent molecule of every ingredient considered, including NG(l), it enabled the gas-phase combustion chemistry occurring near the burning surface to be modeled more realistically than previously possible, and new insights into the factors that control NG(l)'s burning rate and flame structure and these additives' impacts on them were obtained. Evidence for changes in burning rates due to the additives' impacts on radical pool growth were observed, with hydrazine and ammonia inducing the largest such impact. However, the factor found to be most responsible for observed differences in predicted burning rates was the additive's enthalpy.					
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1. Introduction

At its most basic level, the optimization of the performance of a gun or rocket propulsion system fueled with a solid propellant grain (or grains) involves 1) maximizing the amount of stored chemical energy that can be converted into projectile kinetic energy and 2) tailoring the release of that energy so as to maximize its conversion into projectile kinetic energy (Horst 2005). Measures of the amount of stored chemical energy that can be converted into projectile kinetic energy include impetus (I_m) and specific impulse (I_{sp}). The amount of energy that is actually converted into kinetic energy during an interior ballistic cycle is reflected in the area under the pressure versus travel (or time) curve. Constrained by pressure and temperature limits imposed to avoid material failure of system components, the usual objective is to maximize the area.

The problem of designing a propellant grain (or grains) that will maximize the area under the pressure versus travel (or time) curve for a given propulsion system is usually approached by formulating pressurization rates due to the grain's burning in terms of two variables: 1) the linear burning/regression rate (r) of the grain's chemical composition as a function of pressure and 2) the area of the grain's burning surface as burning progresses. The study summarized in this report pertains to the former. Because r is strongly dependent on chemical composition, and given the large number of energetic materials (EMs) with properties that might make them suitable propellant ingredients, one might think that there are limitless possibilities for achieving specific objectives. However, the high costs and risks associated with formulating propellants with "nonconventional" EMs effectively precludes most of them. Therefore, the typical approach is to mix a small amount of a modifier/additive with conventional EMs. For gun and minimum-smoke rocket propellants, conventional EMs include nitrocellulose (NC) and nitroglycerin [NG(*l*)] (which are organic nitrate esters) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (which is an organic nitramine). Examples of the approach abound. A potential application is the "Fastcore" gun propellant concept (Robbins and Worrell 1992; Leveritt et al. 2006), which is based on calculations indicating that laminates with inner and outer layers that burn at significantly different rates have much greater performance potential than current (monolithic) standards. Knowledge of the mechanisms by which modifiers increase or decrease the burning rates of nitrate esters and nitramines would benefit efforts to design such grains.

Seeking means to quantitatively predict the impact modifiers will have on a propellant formulation's burning rate, Miller and Anderson (2000a) developed a semi-empirical mathematical framework to simulate steady-state burning and implemented it in a program they (subsequently) named CYCLOPS (Miller and

Anderson 2004). Derived from general equations for representing the continuities of energy, mass, and species fluxes at a planar condensed-phase–gas-phase interface, and making the assumption that chemical reactions and diffusion in the condensed phase could be neglected, they showed that the one-dimensional (1-D) energy-flux-boundary condition at the interface ($x = 0$) reduced to

$$\left[\lambda_g \frac{dT}{dx} \right]^{+0} = r \rho_c \left(\sum_k^K (Y_g^k)^{-0} (h_g^k)^{+0} - h_c^{-\infty} \right), \quad (1)$$

where the left-hand side of the equation corresponds to the energy flux incident on the interface due to the gas phase's thermal conductivity (λ_g) and the temperature gradient $\left(\frac{dT}{dx}\right)$ at the interface, and the right-hand side corresponds to the energy flux needed to raise the enthalpy of a mass flux with condensed-phase density (ρ_c) from the value for the condensed phase at $x = -\infty$ ($h_c^{-\infty}$) to that of a set of (K total) gas-phase products (k) with mass fractions $(Y_g^k)^{-0}$ and enthalpies $(h_g^k)^{+0}$. The parameters λ_g^{+0} , $\left(\frac{dT}{dx}\right)^{+0}$, and $(h_g^k)^{+0}$ are functions of the temperature of the interface (T^0); λ_g^{+0} and $\left(\frac{dT}{dx}\right)^{+0}$ are also functions of pressure.

A CYCLOPS model comprises the following:

- 1) A detailed, finite-rate chemical kinetics mechanism for simulating the gas-phase combustion chemistry associated with the EM's deflagration, including parameterized formulae for estimating rate coefficients for elementary reactions and thermochemical and transport properties of species involved in those reactions.
- 2) A model/program for simulating steady laminar 1-D burner-stabilized premixed flames at a given pressure (P), inlet/surface gas composition $\left[\{(Y_g^k)^{-0}\}\right]$, inlet mass flow rate ($\dot{M} = r \rho_c A_c$, where A_c is the area of the inlet), and inlet temperature (T^0).
- 3) A formula for calculating the mass flux of the condensed-phase to gas-phase conversion process.
- 4) A method to find the $\dot{M}$ (and thereby $r = \dot{M} / \rho_c A_c$) at which Eq. 1 is satisfied.

Inputs that need to be specified include the EM's condensed-phase enthalpy ($h_c^{-\infty}$), its density (ρ_c) at its starting temperature ($T^{-\infty}$), and the chemical composition of the gas produced by the condensed-phase to gas-phase conversion process for each ingredient (k): $\{(Y_g^k)^{-0}\}_{k'}$.

Developing and applying such models, Miller and Anderson (2000a, 2000b, 2004) were able to reasonably reproduce the burning rates of NG(I), RDX, and four standard nitrate-ester-based gun propellants. Moreover, the corresponding solutions for flame temperature and (rate of) heat release ($\dot{q}$) versus distance from the interface reflected the two-stage structure of flames observed above strands of nitrate esters and nitramines burning in cigarette fashion at low (≤ 20 atm) pressures. At such pressures, visible light emission stands off a distance from the surface that is observable to the naked eye (Fig. 1). The luminous region (typically) corresponds to a near-equilibrium mixture of combustion products. The nonluminous region is commonly referred to as the “dark zone”. Extensively studied (see e.g., Anderson et al. 2011a,b), this phenomenon is understood to occur because nitric oxide (NO) produced by the decompositions of nitrogen dioxide (NO₂) and nitrous acid (HONO) in the primary reaction zone, which is adjacent to the burning surface and raises the temperature on the order of 1000 K, is relatively slow to convert to nitrogen (N₂), delaying the conversion of some of the stored chemical energy into kinetic energy.

As shown schematically in Fig. 1, subsequent to the primary reaction zone, $\dot{q}$ remains relatively modest with increasing distance from the surface until at some point conditions are such that it rapidly increases and the last of the stored energy is released. Producing a marked rise in the gas’s temperature, this phenomenon produces a second prominent feature in the $\dot{q}$ versus distance plot. In this report, the length of the dark zone (d_{DZ}) is defined to be the distance from the surface to the maximum of this feature. (In an actual flame, the onset of visible light may not correspond exactly to this distance.) A temporal parameter is associated with this feature as well: $\tau_{DZ} = \int_0^{d_{DZ}} (v_g)^{-1} dx$, where v_g is the convective velocity of the gas.

One of Miller and Anderson’s key findings was that reactions that were important determinants of d_{DZ} above nitrate esters burning at low (< 300 atm) pressures were also important determinants of nitrate ester burning rates at higher pressures (Anderson et al. 2011a). (The former were identified by performing sensitivity analyses in the dark zone and observing that d_{DZ} was sensitive to changes in the rates of those with relatively large temperature sensitivity coefficients.) As such, it suggested that the burning rates of propellants formulated with nitrate esters might be significantly modified by introducing additives whose decomposition products would accelerate or decelerate the conversion of NO to N₂, and thereby increase or decrease $\left[\lambda_g \frac{dT}{dx} \right]^{+0}$.

Investigating this hypothesis, Miller and Anderson (2000a) calculated regression rates for various NG–additive mixtures burning at 10 atm. The additives

investigated were ammonia (NH_3), formaldehyde (CH_2O), hydrogen (H_2), and N_2 . Because the largest molecules in state-of-the-art chemical kinetics mechanisms at that time had four “heavy” (nonhydrogen) atoms and NG has 15, they modeled the condensed-phase to gas-phase conversion process as an irreversible dissociative phase change to a “nascent product set” (NPS: $\{(Y_g^k)^{-0}\}$), the mass flux of which was computed on the basis of a pyrolysis law (Zenin 1995). Burning rates were presented for three different NPS specifications. (Many others were tested.) The (molar) composition of the NPS that produced burning rates in best agreement with NG(*l*)’s measured values at pressures from 1 to 500 atm was $3\text{HONO}+2\text{HCO}+\text{CO}$.

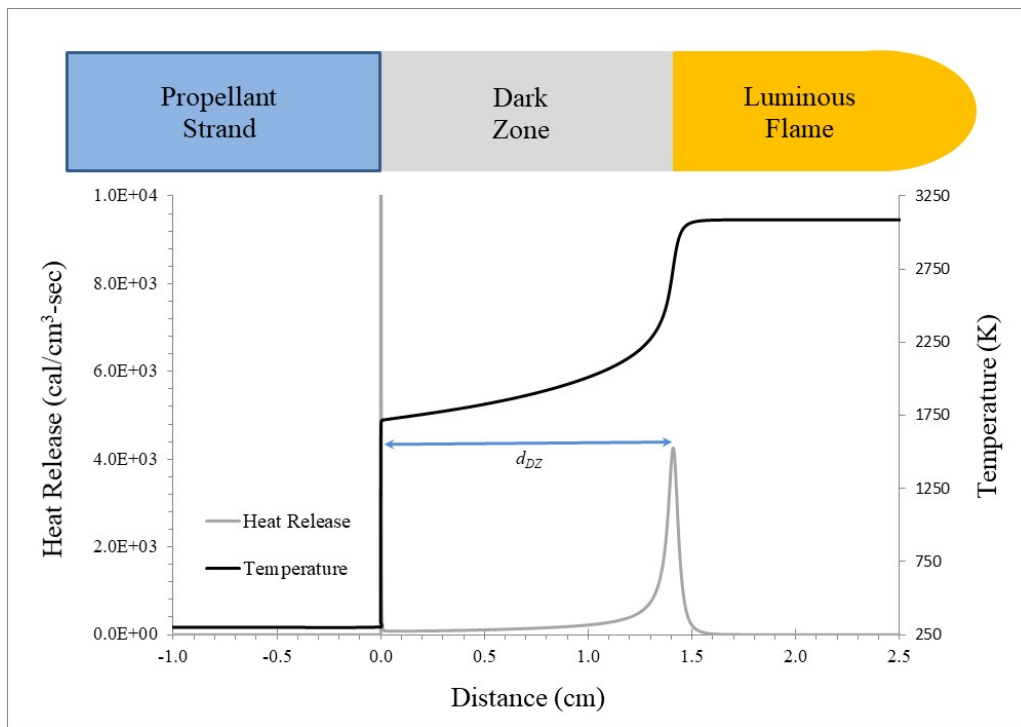


Fig. 1 Schematic diagram illustrating the relationship between the length of the dark zone (d_{DZ}) in a propellant flame that exhibits two-stage structure and the temperature of and heat release ($\dot{q}$) in the gas vs. distance from the propellant’s surface

Miller and Anderson’s interest in NH_3 stemmed from experimental evidence that suggested increases in the burning rates of nitramines produced by doping them with various salts, including triammonium guanidium tetrazolate (TAGzT), were attributable to enhanced conversion of NO to N_2 fostered by the NH_2 produced from NH_3 (Flanagan et al. 1984). NH_3 was also known to be a decomposition product of nitroguanidine (NQ) (Oyumi et al. 1987). NQ is a major ingredient in M30 (a composite triple-base gun propellant), and even at low pressures, flames produced by burning M30 do not exhibit a dark zone.

Comparing the flame structures produced for NG(*l*) and an NG–NH₃ mixture with 10 mol% NH₃, Miller and Anderson observed that, consistent with their speculation regarding its role in “collapsing the dark zone” of M30 flames, the added NH₃ significantly reduced d_{DZ} . In addition, they found the burning rates predicted for an NG–NH₃ mixture with 25 mol% NH₃ were from 14% to 19% higher than those predicted for NG(*l*). (The magnitude of the change in the burning rate depended on the NPS specified for the calculation.) Based on sensitivity analyses, and consistent with the conclusions reached by Flanagan et al. (1984), they attributed the increase in the burning rate to “kinetic activity”^{*} fostered by an increase in the production of NH₂.

These results notwithstanding, Miller and Anderson noted that M30 did not burn faster than single-base propellants and it burned slower than double-base propellants. This prompted them to speculate about the importance of other factors, including the fact that NQ could produce a lower flame temperature/cooling effect. They also found that the model’s predictions were sensitive to the specification of NH₃’s $h_c^{-\infty}$. These factors are considered in more detail in this report.

Miller and Anderson viewed NG–N₂ as a “control”, with their strong expectation being that N₂ would not react chemically but, acting as a diluent/heat sink, reduce NG(*l*)’s burning rate. Burning rate predictions were not presented for the mixture, but consistent with their expectation, they reported that $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$ in the solution for NG–N₂ was 28% less than that in the comparable solution for NG(*l*).

Miller and Anderson were interested in the effect CH₂O would have on NG(*l*)’s burning rate because it is a ubiquitous intermediate in C/H/N/O combustion chemistry. Thinking that, like N₂, it would simply act as a diluent/heat sink, they expected the NG–CH₂O mixture they specified to have a burning rate similar to

^{*} In the governing equations of CYCLOPS models, there are a number of terms that, being explicit functions of species concentrations, will change when a burning-rate modifier is added to a formulation and thus have some potential to change the formulation’s burning rate. However, based on our experience, the only terms of the model employed for this study that, via small changes in species concentrations, have the potential to change significantly enough to effect a nonnegligible burning rate change are the rates (R_i) by which species are produced or consumed via chemical reactions (i) and $h_c^{-\infty}$. The potentials of R_i to be changed by small changes in species concentrations stem from their sensitivity to changes in temperature. Expressed through the reaction rate coefficients (k_i) employed to compute them (see Section 2.1), this sensitivity affords a mechanism that we refer to herein as “kinetic activity”. It supposes that the burning-rate modifier increases (to first order) the concentrations of some species, and thereby directly increases the R_i of a subset of reactions within the network. In isolation, the effect of these increases might be negligible. However, if they effect a change in $\dot{q}$, and thereby the system’s temperature, that effect has the potential to be amplified by the remainder of the network. Since radicals (i.e., atoms and molecules with an unpaired electron) tend to react much more quickly and exothermically than closed-shell species, modifiers that are effective in changing the rate of their production (or destruction) will tend to have more potential to impact burning rates than those that are not. Modifier-induced changes in the rates of highly exothermic reactions also have the potential to effect nonnegligible changes in burning rates.

NG–N₂'s. However, it burned at about the same rate as NG(*l*). (There were small differences between results produced with different NPSs.)

Miller and Anderson (2004) subsequently demonstrated that the CYCLOPS framework could be extended to produce reasonable flame structures and burning rate predictions for systems with multiple EM ingredients. Specifying NPSs for individual EMs (based on the same empirical approach they employed in their previous study of NG(*l*)'s and RDX's deflagrations) and combining them in proportion to the EMs' mass fractions in the NC-based gun propellants M10, M2, M9, and JA2, they were able to reasonably reproduce each of their measured burning rates.

In a subsequent CYCLOPS-based study, Conner et al. (2008) investigated the impacts that an expanded list of additives would have on the burning rates and flame structures produced by a model constructed to simulate the deflagration of 13.15 wt%N NC. The list included hydrazine (N₂H₄), hydrazoic acid (HN₃), and isocyanic acid (HNCO). Conner et al.'s interest in N₂H₄ stemmed from simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) results reported by Hayden et al. (2006). Those results indicated that N₂H₄ rather than NH₃ was responsible for the large increases observed in the burning rates of RDX and 1,3,5,7-tetranitro-1,3,5,7-tetrazoctane (HMX) when they were doped with TAGzT (Flanagan et al. 1984). HN₃ was of interest because it was observed to be a product of the thermal decomposition of 5-aminotetrazole (Brill and Ramanathan 2000; Kiselev and Gritsan 2009), and azides had been observed to increase the burning rate of HMX (Flanagan et al. 1984). HNCO was of interest because it had been observed as a product of the pyrolysis of urea [H₂NC(O)NH₂] (Chen and Isa 1998), DINGU (Oyumi and Brill 1988), and compounds that were being investigated as burning rate modifiers for ammonium-perchlorate-based rocket propellants (Williams et al. 1994). Urea had been proposed as an additive for reducing the amount of nitrogen oxides (NO_x) produced by the combustion of gun propellants (Pesce-Rodriguez et al. 1996). Preliminary results reported by Miller and Anderson (2000b) for an NG–HNCO mixture burning at 10 atm indicated HNCO would act as burning-rate suppressant and reduce d_{DZ} .

Conner et al.'s expectations for the impact each additive would have on NC's burning rate were met for every case except NH₃. Based on Miller and Anderson's (2000a) results for NG(*l*) and NG–NH₃, they had expected NH₃ would increase NC's burning rate. But at pressures from 10 to 1000 atm, the rates computed for NC–NH₃ were lower. (At higher pressures, the rates computed for the two systems were approximately the same.) Conner et al. did not, however, consider their results conclusive; they recommended the parameterizations of rate coefficient formulae

for some reactions be validated and that the chemical kinetics mechanism be examined to determine if any potentially important reactions were missing from it.

This report summarizes a study that was undertaken to 1) address issues raised in the studies mentioned, 2) conduct more comprehensive analyses of the additives' impacts on nitrate ester flame chemistry, and 3) investigate their impacts at a gun combustion chamber-relevant pressure (2000 atm). Having developed a detailed finite-rate chemical kinetics mechanism for modeling the combustion of gaseous NG [NG(g)] that included well-founded parameters for computing the rates of elementary reactions involving the parent molecule and large daughters of its decomposition (Chen et al. 2019a), and having shown that coupled with the CYCLOPS framework it reasonably reproduced measured NG(l) burning rates when $(Y_g^{NG})^{-0}$ was 1, we chose NG(l) as the baseline system. To ensure the combustions of N₂H₄, HN₃, and urea were well simulated, some additional mechanism development was undertaken. For continuity and comparison with prior CYCLOPS-based studies, predictions were also obtained with a mechanism that was very similar to mechanisms employed by Miller, Anderson, and coworkers subsequent to the studies published in 2000 (Anderson et al. 2011a).

Burning-rate and flame-structure predictions produced for NG(l) and NG-additive mixtures are presented, compared, and discussed. A number of results were surprising. Explanations are proffered.

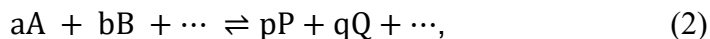
2. Modeling and Analysis Considerations

2.1 Burning-Rate Predictor: CYCLOPS

The mathematical framework underlying CYCLOPS is described in detail elsewhere (Miller and Anderson 2000a). The implementation employed for this study was the one developed and employed previously by Miller and Anderson. Formulation-specific inputs included 1) detailed finite-rate chemical kinetics mechanisms, 2) the ingredients' condensed-phase densities and specific enthalpies, 3) NPS specifications for the condensed-phase to gas-phase conversion process for each ingredient, and 4) a formula for computing the mass flux of that process as a function of the surface/inlet temperature.

2.1.1 Detailed Finite-Rate Chemical Kinetics Mechanisms

A detailed finite-rate chemical kinetics mechanism is a network comprising molecular and/or atomic species (k) connected by elementary reactions (i)



where $a, b, \dots$, are stoichiometric coefficients for species A, B, $\dots$, respectively. It specifies parameters for calculating (molar) rates of species conversion (R_i),

$$R_i = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt} = \dots = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \dots, \quad (3)$$

via the law of mass action,

$$R_i = k_i[A]^a[B]^b \dots - k_{-i}[P]^p[Q]^q \dots, \quad (4)$$

where k_i and k_{-i} are forward and reverse rate coefficients, respectively (Benson 1976). For reactions for which it is assumed interactions with “third-bodies” will not affect their rate, k_i in mechanisms developed and employed by our group are computed with a modified form of the Arrhenius equation,

$$k_i(T) = A_i T^{n_i} \exp\left(\frac{-E_{a,i}}{R_u T}\right), \quad (5)$$

where A_i , n_i , and $E_{a,i}$ are reaction-specific constants and R_u is the universal gas constant. For reactions for which such interactions cannot be neglected, pressure-dependent “corrections” are integrated with this basic functional form to specify $k_i(T, P)$ (formulae) that account for them. Governing equation source terms computed on the basis of this formalism include species molar conversion rates ($\dot{\omega}_k$),

$$\dot{\omega}_k = \sum_i^I (v_{ki}'' - v_{ki}') R_i, \quad (6)$$

where (for a mechanism with I reactions) v_{ki}'' (v_{ki}') are the stoichiometric coefficients for i 's products (reactants). The $\dot{q}$ reported herein were computed per

$$\dot{q} = -\sum_k^K \dot{\omega}_k h_g^k W_k, \quad (7)$$

where h_g^k is species k 's gas-phase specific enthalpy and W_k is its molecular weight.

Two detailed finite-rate chemical kinetics mechanisms were assembled and employed for this study. They are referred to hereafter as DZ (for dark zone) and PM (for “parent molecule”). The DZ mechanism was a subset of the PM mechanism. A complete description of the PM mechanism will be provided in a separate report (Chen et al. 2019a). The following provides an overview of the DZ and PM mechanisms’ geneses and differences.

The starting point/core of the DZ mechanism was a mechanism constructed by Anderson et al. (2011a). Comprising parameters for computing the rates of 368 reversible elementary reactions and thermochemical and transport properties for 58 species, it had been critically evaluated with respect to its ability to reproduce

experimentally measured characteristics of flames produced by the combustion of EMs formulated with nitrate esters and/or nitramines. Dark zone formation and structure was a particular focus. It is also relevant to note that the starting point for that mechanism was the mechanism Miller and Anderson employed to calculate burning rates for nitrate ester-based gun propellants (Miller and Anderson 2004). Most of the subsequent revisions to that mechanism pertained to reactions involving species with N_xH_y stoichiometries, and dark zone pertinent results produced by the 2011 version were very similar to those produced by the 2004 version (Anderson et al. 2011a). Thus, the 2011 version (and therefore DZ's core) is considered very similar to the mechanism employed for the 2004 study and those that followed. The mechanisms that were bases for CYCLOPS-based studies published prior to 2004 are not.

From there, our interest in N_2H_4 motivated us to obtain better-founded parameters for computing the pressure-dependent rate of the third-body induced (fall-off) reaction for breaking its N–N bond: $N_2H_4 + M = NH_2 + NH_2 + M$. Our desire to model the impact of adding HN_3 and consideration of a study published by Grams and Sausa (2011) prompted us to include parameters for computing the rates of nine reversible elementary reactions and thermochemical and transport properties for three additional species. Finally, a (sub)mechanism for simulating the decomposition of urea was built on the basis of quantum mechanics (QM)-based electronic structure methods, statistical mechanics, and transition state theories. Comprising parameters for computing the rates of 77 reversible elementary reactions and thermochemical and transport properties for 14 additional species, this mechanism will be summarized in a separate publication (Chen and McQuaid 2019b). All together, the DZ mechanism comprised parameters for computing the rates of 454 reversible elementary reactions and thermochemical and transport properties for 75 species.

The starting point for the PM mechanism was a set of parameters for computing the rates of 1) reactions involving $NG(g)$ and large daughters of its decomposition that were derived from results produced by QM-based electronic structure methods, statistical mechanics, and transition state theories (Chen et al. 2019a), 2) reactions in a mechanism for modeling monomethylhydrazine–red fuming nitric acid (MMH–RFNA) combustion (Anderson et al. 2010); 3) reactions involving methoxide (CH_3O), methanol (CH_3OH), ethoxide (C_2H_5O), and ethanol (C_2H_5OH) that were in a mechanism for modeling *n*-heptane oxidation (Mehl et al. 2011), and 4) reactions in a mechanism developed to model the combustion of methyl and ethyl nitrate (Chen and McQuaid 2013). For this study, we added the data that were added to the DZ mechanism to ensure the combustions of N_2H_4 , HN_3 , and urea were well simulated. All together, the PM mechanism comprised parameters for

computing the rates of 1075 reversible elementary reactions and thermochemical and transport properties for 189 species.

We note that to facilitate the discussion of individual reactions, all have been written herein so that the forward reaction corresponds to the one that was found to be dominant. In addition, in some of the tables and figures in this report, some species have names/labels that are not sufficient for establishing their molecular structure. Therefore, a look-up table is provided for that purpose in Appendix A.

2.1.2 Properties of Condensed Phase Mixtures

2.1.2.1 Ingredient Properties

The additives investigated in this study were NH_3 , N_2 , N_2H_4 , HNCO , HN_3 , CH_2O , and urea. Considering delineation of the impact of factors such as condensed-phase interactions between ingredients, the condensed phase's bulk temperature ($T^{-\infty}$), and the pressure dependence of mixture densities (ρ_c) to be beyond the study's scope, at its outset we only anticipated obtaining results for one set of $\rho_c^{k'}$ and $h_c^{k'}$ for each ingredient (k'), and computing ρ_c and $h_c^{-\infty}$ per

$$\frac{1}{\rho_c} = \sum_{k'}^{K'} \frac{Y_c^{k'}}{\rho_c^{k'}}, \quad (8)$$

and

$$h_c^{-\infty} = \sum_{k'}^{K'} (Y_c^{k'} h_c^{k'})^{-\infty}, \quad (9)$$

respectively. In addition, we wanted the properties of the mixtures to be “physically realistic” even though most (if not all) would not be stable at 298 K and 1 atm. The sets that followed from these judgements are listed in Table 1. For N_2H_4 , HN_3 , CH_2O , and urea, which are condensed-phase materials at 298 K and 1 atm, the $\rho_c^{k'}$ and $h_c^{k'}$ were specified based on values found via an internet search. (Most were not “citable,” but generally we found several values from different sources that corroborated the reasonableness of the values specified.) For NH_3 , N_2 , and HNCO , which are gases at 298 K and 1 atm, we specified $\rho_c^{k'}$ to be equal to the density of their liquid phase at their normal boiling point, and their $h_c^{k'}$ to be equal to their $h_g^{k'}$ at 298 K.

Most of the analyses performed for this study involved data from simulations produced with the $h_c^{k'}$ listed in Table 1. As such, those simulations represent (and are referred to as) “baseline” solutions. In the course of writing this report, simulations were performed with alternate $h_c^{k'}$ values specified to observe r 's dependence on them and to facilitate comparison of the additives' kinetic activities.

(See Section 3.5.) Additional analyses of the results produced with alternate $h_c^{k'}$ might have been instructive, but we could not afford to undertake them.

Table 1 Ingredient properties

Ingredient	Stoichiometry	Mol Wt (g/mol)	BP (K)	ρ_c (g/cm ³)	$h_c^{-\infty}$ (kcal/mol)	$h_c^{-\infty}$ (cal/g)
NG(<i>l</i>)	C ₃ H ₅ N ₃ O ₉	227.1	323	1.59	−89.6	−395
HN ₃	H ₁ N ₃	43.0	310	1.09	71.9	1672
N ₂ H ₄	H ₄ N ₂	32.0	387	1.02	22.8	712
NH ₃	H ₃ N ₁	17.0	240	0.64	−10.9	−643
HNCO	C ₁ H ₁ N ₁ O ₁	43.0	297	1.20	−28.2	−656
N ₂	N ₂	28.0	77	0.81	0	0
CH ₂ O	C ₁ H ₂ O ₁	30.0	254	0.80	−41.6	−1387
urea	C ₁ H ₄ N ₂ O ₁	60.0	423(d)	1.32	−79.6	−1327

2.1.2.2 Mixture Properties

The properties specified for each mixture followed from the NG:additive (molar) ratio specified for it. Those specifications were based on considerations discussed by Miller and Anderson (2000a). Concerned that differences in final (adiabatic) flame temperatures (T_{AD}) would compromise their ability to draw conclusions from the comparison of results for different mixtures, they specified a ratio for each mixture that yielded an equivalence ratio equal to 1.0; that is, stoichiometric to a product set comprising CO₂, H₂O, and N₂. The choice to make mixtures stoichiometric was “rational” because NG is slightly fuel lean (C₃H₅N₃O₉ → 3CO₂+2.5H₂O+0.5O₂+1.5N₂) and all the additives they were considering (except N₂) were fuel rich. The ratios corresponding to this target are listed in Table 2. Because NG–N₂ cannot be made stoichiometric, we selected the molar ratio for it (3.5:1) based on the observation that five of the other seven mixtures had ratios between 3:1 and 4:1.

Table 2 also lists other (calculated) properties for each mixture, including their ρ_c , $h_c^{-\infty}$, T_{AD} , I_m , and I_{sp} . The T_{AD} were computed with the STANJAN equilibrium program packaged with a pre-commercial version of CHEMKIN-III (Kee et al. 1996) distributed to us by Sandia National Laboratories (Livermore, California). The DZ and PM mechanisms’ library for computing species thermodynamic properties was employed for the calculations. The I_m and I_{sp} values were calculated with CHEETAH 8.0 (LLNL 2015). The Blake thermodynamics property library packaged with it was employed for the I_m calculations. Values corresponding to a loading density of 0.2 g/cm³ are presented. The JCZS thermodynamics property

library was employed for the I_{sp} calculations. The table presents shifting equilibrium values produced by a rocket calculation with the chamber pressure specified to be 68 atm and the exhaust pressure specified to be 1 atm. The $\rho_c^* I_{sp}$ for all mixtures except NG–N₂ fell within 2% of 407 g-s/cm³.

Table 2 Mixture properties^a

Mixture	Molar ratio	Mass fractions	ρ_c	$h_c^{-\infty}$	T_{AD}		I_m	I_{sp}	$\rho_c^* I_{sp}$
			g/cm ³	cal/g	10 atm	2000 atm	J/g	sec	g-s/cm ³
NG(<i>l</i>)	...	...	1.59	−395	3087	3629	1145	258	410
NG–HN ₃	1:1	0.841:0.159	1.48	−66	3186	3775	1271	270	400
NG–N ₂ H ₄	4:1	0.966:0.034	1.56	−357	3115	3671	1205	265	413
NG–NH ₃	3:1	0.976:0.024	1.54	−401	3086	3623	1190	263	408
NG–NH ₃ –HNCO	6:1:1	0.958:0.012:0.030	1.55	−405	3087	3628	1170	261	405
NG–N ₂	3.5:1	0.966:0.034	1.54	−381	3063	3581	1129	256	394
NG–HNCO	3:1	0.941:0.059	1.55	−410	3087	3632	1151	259	401
NG–CH ₂ O	4:1	0.968:0.032	1.54	−426	3093	3644	1164	261	402
NG–urea	6:1	0.958:0.042	1.58	−434	3067	3594	1155	260	411

^a See Section 2.1.2.2 for details concerning the calculations of the listed properties.

2.1.3 Condensed-Phase to Gas-Phase Conversion Process

2.1.3.1 Pyrolysis Law

As in the studies by Miller and Anderson (2000a, 2004) and Conner et al. (2008), the condensed-phase to gas-phase conversion process was modeled as an irreversible step that produced a gaseous mass flux ($\dot{m} = \dot{M}/A_c$) with a magnitude computed on the basis of a pyrolysis law,

$$\dot{m} = A_s \exp\left(-\frac{E_s}{R_u T}\right), \quad (10)$$

with $A_s = 1.800 \times 10^3$ g/cm²s and $E_s = 9935$ cal/mol (Zenin 1995). These values have been found to be appropriate for a wide range of nitrate ester propellants.

2.1.3.2 Nascent Product Sets

The chemical composition of the $\dot{m}$ produced by a given mixture was computed by mass-fraction weighting the NPSs that were specified for each ingredient. The NPSs are shown in Table 3. The mechanism development work discussed in Section 2.1.1 enabled the NPSs for all the additives to correspond to a nondissociative phase change of the parent: $Y_{add}^0 = 1$. (Although it is tempting to

refer to the process as evaporation or sublimation, either would be a misnomer because, as formulated, the pyrolysis law corresponds to an irreversible step while “true” evaporation and sublimation are reversible processes.) For urea, a second NPS corresponding to a (single-step) dissociative phase change to NH_3 and HNCO was also specified (Chen and Isa 1998). (For discussion purposes, this NPS is associated with an ingredient named “urea–spv2”, where “spv2” stands for “surface product variation 2”.) For $\text{NG}(l)$, two specifications were employed. For calculations in which the DZ mechanism was employed, the specification (NPS-1) was the same as that specified by Miller and Anderson (2004) for their CYCLOPS-based study of nitrate ester propellant deflagration. NPS-1 was also specified for a set of calculations performed with the PM mechanism. For a second set of calculations performed with the PM mechanism, the specification (NPS-2) corresponded to a nondissociative phase change: $Y_{\text{NG}(g)}^{-0} = 1$.

Table 3 Nascent gas-phase products of condensed-phase to gas-phase conversion of individual ingredients

Ingredient (c-phase)	Nascent gas-phase products	
	NPS-1	NPS-2
$\text{NG}(l)$	$2.6 \text{ NO}_2 + 0.4 \text{ HONO} + 2.0 \text{ CH}_2\text{O} + 0.6 \text{ HCO} + 0.4 \text{ CO}$	$\text{NG}(g)$
HN_3	HN_3	HN_3
N_2H_4	N_2H_4	N_2H_4
NH_3	NH_3	NH_3
N_2	N_2	N_2
HNCO	HNCO	HNCO
CH_2O	CH_2O	CH_2O
urea	$\text{H}_2\text{NC}(\text{O})\text{NH}_2$	$\text{H}_2\text{NC}(\text{O})\text{NH}_2$
urea–spv2	$\text{NH}_3 + \text{HNCO}$	$\text{NH}_3 + \text{HNCO}$

2.1.4 Flame Simulations

Steady laminar 1-D burner-stabilized premixed flame simulations were performed with a slightly modified version of PREMIX (Kee et al. 1985). Parameters pertaining to grid selection and convergence criteria for the Newton method search for solutions were selected to yield results with an absolute precision of about 1% and a relative precision of about 0.5%. Thus, we assume numerical uncertainty is excluded as a possible explanation for differences between predicted burning rates that exceed 1%.

2.2 Analysis

2.2.1 Sensitivity Analyses

As discussed by Miller and Anderson (2000a, 2004), insight into the mechanisms by which an additive impacts an EM's burning rate can be obtained by computing and analyzing first-order sensitivity coefficients for the solution at the grid point adjacent to the burning surface ($x = 0$). Referred to hereafter as the 2nd grid point, this location is particularly significant because it is the primary determinant of $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$, and, therefore, the burning rate. Presented here are (logarithmic-derivative form) normalized temperature sensitivity coefficients (S_i),

$$S_i = \frac{A_i}{T_m} \frac{\partial T}{\partial A_i}, \quad (11)$$

where A_i is the pre-exponential factor of the rate coefficient formula for reaction i (Eq. 5), T is the temperature at the grid point, and T_m is the maximum temperature in the computational domain. As will be appreciated by inspection of Eq. 11, a positive S_i indicates that increasing A_i would have increased T and, therefore, dT/dx (and the burning rate). We (generally) assume a reaction's $|S_i|$ relative to all other $|S_i|$ reflects its importance in the deflagration process. We also assume that relative $|S_i|$ values reflect the reactions' impacts on $\dot{q}$ (McQuaid 2013).

2.2.2 Pathway Diagrams

To gain additional insight into the impact each additive had on NG(g)'s combustion chemistry, we employed programs (named PREAD and Elemap) developed by Anderson and coworkers to postprocess PREMIX-generated data and create diagrams illustrating the relative rates of reaction by which important species decomposed and/or formed. Primarily interested in the reaction chemistry near the burning surface, we produced diagrams corresponding to the 2nd grid point for all the baseline solutions presented in this report. For selected cases, diagrams corresponding to locations downstream of the 2nd grid point were also produced and analyzed.

3. Results and Discussion

3.1 Calculated Burning Rates for NG(*l*) and NG-Additive Mixtures: Baseline Cases

3.1.1 10 atm

Table 4 lists regression rates calculated for the baseline NG(*l*) and NG-additive mixtures burning at 10 atm. Figure 2 presents the data graphically. Figure 2a compares absolute values produced by each mechanism/NPS model. Figure 2b compares (on a model-by-model basis) mixture burning rates relative to the rate calculated for NG(*l*) with the same model.

Considering first the results produced for NG(*l*), we note that all three mechanism/NPS models produced a burning rate in reasonable agreement with the nominal measured value. (We consider the agreement between calculated and measured values to be reasonable if they are within a factor of 2 of one another.) As mentioned in Section 2.1.1, DZ/NPS-1 was very similar to the mechanism/NPS combination Miller and Anderson (2004) employed to calculate burning rates for NG(*l*): the models' mechanisms were slightly different and their NPSs were identical. Therefore, the similarity of the burning rates they produced (1.1 cm/s and 0.9 cm/s, respectively) and their agreement with the measured rate was not surprising.

The same can be said about the result produced by PM/NPS-1. Although the PM mechanism as a whole was significantly different than the DZ mechanism, the small-molecule reaction networks in them were very similar and it is not hard to imagine that molecules with more than four heavy atoms would not readily form in a burner-stabilized flame produced by combusting an inlet gas comprising $2.6\text{NO}_2 + 0.4\text{HONO} + 2.0\text{CH}_2\text{O} + 0.6\text{HCO} + 0.4\text{CO}$.

The same cannot be said about the burning rate predicted by PM/NPS-2. The specification of NG(*g*) as the nascent product of the condensed-phase to gas-phase conversion process required the molecular system to evolve through O-NO₂, C-H, and C-C bond-breaking steps that were not in the DZ mechanism. Indeed, knowing that the specification of NPS-1 effectively bypassed bond-breaking steps that might not be fast, suspecting that the concentration of formyl radical (HCO) specified in NPS-1 was unrealistically high for a radical near the burning surface of a propellant, and knowing that reactions involving HCO are very fast and exothermic, we were somewhat surprised that the burning rate predicted by PM/NPS-2 was similar to those predicted by DZ/NPS-1 and PM/NPS-1 and close to the measured value. (Had it been significantly different, it would have called into question the validity of NPS-2.)

Table 4 Predicted burning rates for NG(*l*) and NG–additive mixtures: 10 atm

Mixture	<i>r</i> (cm/s)						
	Measured ^a	DZ/NPS-1		PM/NPS-1		PM/NPS-2	
		Predicted	ρ -normalized ^b	Predicted	ρ -normalized ^b	Predicted	ρ -normalized ^b
NG(<i>l</i>)	0.75	1.08	1.08	0.92	0.92	0.69	0.69
NG–HN ₃	...	2.87 [+170%]	2.67 [+150%]	2.72 [+200%]	2.53 [+175%]	2.52 [+270%]	2.35 [+240%]
NG–N ₂ H ₄	...	1.79 [+66%]	1.76 [+63%]	1.60 [+74%]	1.57 [+71%]	1.31 [+90%]	1.28 [+86%]
NG–NH ₃	...	1.08 [+0%]	1.05 [–3%]	0.95 [+3%]	0.92 [+0%]	0.81 [+17%]	0.78 [+13%]
NG–NH ₃ –HNCO	...	0.97 [–10%]	0.95 [–12%]	0.85 [–8%]	0.83 [–10%]	0.72 [+4%]	0.70 [+1%]
NG–N ₂	...	0.97 [–10%]	0.94 [–13%]	0.83 [–10%]	0.80 [–13%]	0.64 [–7%]	0.62 [–10%]
NG–HNCO	...	0.84 [–22%]	0.82 [–24%]	0.74 [–20%]	0.72 [–22%]	0.62 [–10%]	0.60 [–13%]
NG–CH ₂ O	...	0.78 [–28%]	0.76 [–30%]	0.68 [–26%]	0.66 [–28%]	0.55 [–20%]	0.53 [–23%]
NG–urea	...	0.63 [–42%]	0.63 [–42%]	0.57 [–36%]	0.57 [–36%]	0.52 [–24%]	0.52 [–24%]
NG–urea–spv2	...	0.62 [–43%]	0.62 [–43%]	0.54 [–41%]	0.54 [–41%]	0.48 [–30%]	0.48 [–30%]

^aMiller and Anderson (2004).^b $r(\rho\text{-normalized}) = r(\text{predicted}) * \rho(\text{mixture}) / \rho(\text{NG}(\textit{l}))$.

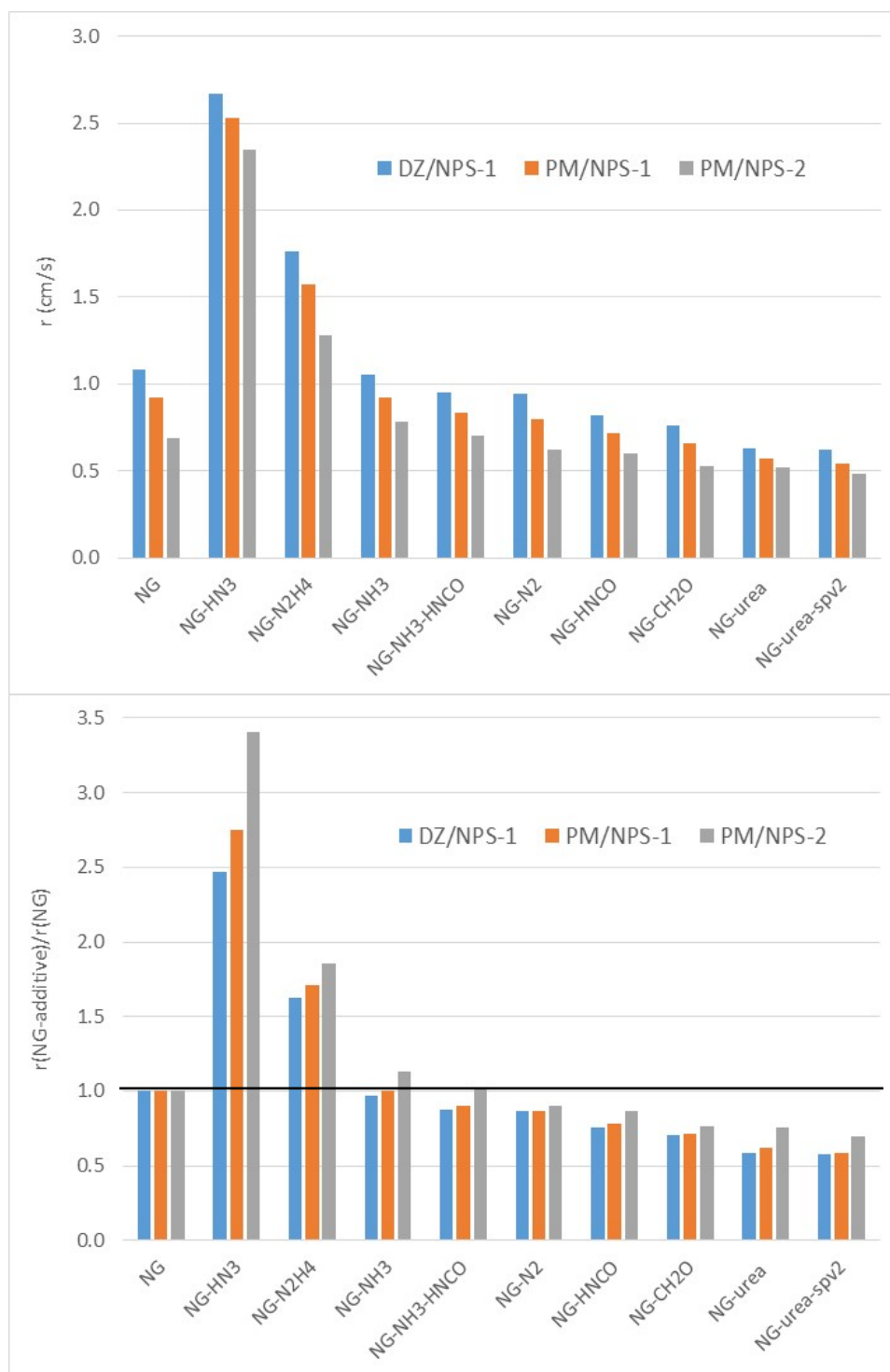


Fig. 2 Predicted regression rates (r) for NG(l) and NG-additive mixtures burning at 10 atm: a) ρ_c -normalized absolute rates; b) rates relative to $r[\text{NG}(\textit{l})]$

One reason the burning rate produced by PM/NPS-2 was similar to the ones produced by DZ/NPS-1 and PM/NPS-1 was that, in the range of temperatures predicted for the surface, the enthalpy of NPS-1 $[\sum_k^K (Y_g^k)^{-0} (h_g^k)^{+0}]$ was much higher than that of NG(g). As shown in Table 5, on the basis of the double-base pyrolysis law formulated by Zenin (1995), the ρ_c of NG(l) (1.59 g/cm³), and NG(l)'s measured burning rate at 10 atm (0.75 cm/s), the temperature of NG(l)'s burning surface is 683 K. At 683 K, the enthalpy of NPS-1 is -87 cal/g; NG(g)'s is -212 cal/g. As a result, the $[\lambda_g \frac{dT}{dx}]^{+0}$ necessary to sustain the production of NPS-1 under these conditions would be 366 cal/cm²s while that necessary to sustain the production of NG(g) would be only 217 cal/cm²s. (The differences between the $[\lambda_g \frac{dT}{dx}]^{+0}$ predictions produced by the NPS-1- and NPS-2-based models at the burning rates they predicted were even larger. See Table 5.) Therefore, even though NPS-2 did not have the potential to react as quickly and exothermically as NPS-1, in the temperature range of interest, it did not need it to produce a comparable mass flux since the energy flux needed to convert a unit mass flux of NG(l) to NG(g) was much lower than that needed to convert a unit mass flux of NG(l) to NPS-1.

Table 5 Comparisons of Eq. 1 parameters for different mechanism/NPS models: NG(l) burning at 10 atm

Mechanism	NPS	r	T^0	$\sum_k^K (Y_g^k)^{-0} (h_g^k)^{+0}$	$[\lambda_g \frac{dT}{dx}]^{+0}$
		cm/s	K	cal/g	cal/cm ² s
...	NPS-1	0.75 ^a	683 ^b	-87	370
...	NPS-2	0.75 ^a	683 ^b	-212	220
DZ	NPS-1	1.08	719	-76	550
PM	NPS-1	0.92	703	-81	460
PM	NPS-2	0.69	675	-214	200

^aNominal measured value.

^bCalculated based on the nominal measured r and Zenin's (1995) pyrolysis law for double-base propellants.

We note that this finding also speaks to intuiting an additive's potential for modifying a formulation's burning rate. That is, it is not just the reactive potential of it and/or its nascent products that one should consider. Rather, it is that potential *relative* to any change in the energy flux required to convert the (modified) formulation into a gas that will ultimately determine the burning rate change.

With respect to the results produced for NG-additive mixtures, Fig. 2 makes clear that the relative changes in the burning rates produced by the three mechanism/NPS models were similar, and it reveals some trends. As shown in Fig. 2a,

$r(\text{DZ/NPS-1}) > r(\text{PM/NPS-1}) > r(\text{PM/NPS-2})$ for each mixture, but when the results were “normalized” with respect to the burning rate the same mechanism/NPS model produced for NG(*l*), the opposite trend was observed. Regardless, from the standpoint of comparing the net impacts the additives had on NG(*l*)’s burning rate, these trends do not change the ordering of the mixtures’ burning rates and, therefore, are not further discussed.

All three mechanism/NPS models yielded burning rate predictions for NG–HN₃ and NG–N₂H₄ that were significantly higher than those they produced for NG(*l*). PM/NPS-2’s (ρ_c -normalized) burning rate prediction for NG–HN₃ was about 240% higher than its prediction for NG(*l*), and its prediction for NG–N₂H₄ was about 86% higher than its prediction for NG(*l*). Both of these increases greatly exceed any (hypothetical) additive-induced increase observed in prior CYCLOPS-based studies.

The results for NG–NH₃ also merit comment. PM/NPS-2’s burning-rate prediction for it was 13% higher than its prediction for NG(*l*). This result is similar to one Miller and Anderson (2000a) produced with a different NPS (3HONO+2HCO+CO). However, after shortcomings of the mechanism that was the basis for that study were identified and corrected, they found that NG(*l*)’s burning rate was not well reproduced when that NPS was coupled with the revised mechanism (Miller and Anderson 2004). They resolved that issue by specifying NPS-1 (2.6NO₂+0.4HONO+2.0CH₂O+0.6HCO+0.4CO). But as mentioned in the introduction, when Conner et al. (2008) employed a small-molecule NPS (2.9NO₂+1.1HCO+2.2CH₂O+1.1CH₂+2.2CO+0.4H) and a mechanism similar to the corrected one (and DZ’s core) to simulate the burning of 13.15 wt%N NC, the model predicted the addition of NH₃ would slightly suppress NC’s burning rate at 10 atm. Similarly, as shown in Table 4, DZ/NPS-1’s and PM/NPS-1’s burning rate predictions for NG–NH₃ and NG(*l*) were about the same.

Given Flanagan et al.’s (1984) results and conclusions, we consider PM/NPS-2’s prediction for the impact of NH₃ on NG(*l*)’s burning rate credible. Indeed, coupled with Conner et al.’s (2008) finding and DZ/NPS-1’s and PM/NPS-1’s failures to predict a higher burning rate for the mixture, it suggested to us that the time/length scale of NH₃’s decomposition relative to that of NO’s production from the decomposition of NO₂ was an important factor in NH₃’s ability to influence a nitrate ester’s burning rate. Results corroborating this hypothesis are presented and discussed in Section 3.3.

Comparisons of the burning rates predicted for NG–urea, NG–urea–spv2, and NG–NH₃–HNCO were also revealing. Although ostensibly positing different condensed-phase additives, the only difference between the calculations performed

to predict the burning rates of NG–urea and NG–urea–spv2 was the specification of the mixtures' NPS: urea (gas) and HNCO+NH₃, respectively. The specifications for their $h_c^{-\infty}$ and ρ_c were the same. All three mechanism/NPS models predicted burning rates for NG–urea and NG–urea–spv2 that were significantly lower than they predicted for NG(*l*), and NG–urea–spv2's were slightly lower than NG–urea's. Given that NG–NH₃'s burning rate was slightly higher than NG(*l*)'s and NG–HNCO's was slightly lower, one might have guessed that NG–urea–spv2's would be similar to NG(*l*)'s. That did not occur because the mixture's $h_c^{-\infty}$ was much lower than NG(*l*)'s. (See Section 3.5.) As for the slight differences in the burning rates predicted for NG–urea–spv2 and NG–urea, like the difference in the results produced for NG(*l*) with different NPSs specified, the lower rates predicted for NG–urea–spv2 appear to have been primarily due to the greater energy flux needed to convert (solid) urea to HNCO+NH₃ versus that needed to convert it to urea (gas). In the solutions produced by PM/NPS-2, T^0 was 650 K for NG–urea and 643 K for NG–urea–spv2. At these temperatures, the specific enthalpies of the NPSs were –245 cal/g and –238 cal/g, respectively, with the difference in T^0 being a factor that mitigated the difference.

The only differences in the inputs for the NG–NH₃–HNCO and NG–urea–spv2 simulations were the mixtures' $h_c^{-\infty}$: –405 cal/g versus –434 cal/g, respectively. Given that the heat capacity of NG(*l*) is approximately 0.3 cal/g-K, the difference between $h_{NG-NH_3-HNCO}^{-\infty}$ and $h_{urea-spv2}^{-\infty}$ was approximately equivalent to a 100-K difference in $T^{-\infty}$. The equivalence between $h_c^{-\infty}$ and $T^{-\infty}$ within the CYCLOPS framework, its concomitant influence on the difference between $h_c^{-\infty}$ and h_{NPS}^0 , and the resulting impact on burning rate predictions was previously noted in a study of the deflagration of ammonium perchlorate (McQuaid and Chen 2014; Chen and McQuaid 2014). Considered from this perspective, the large difference between the (ρ_c -normalized) burning rates computed for the two systems (0.48 cm/s versus 0.70 cm/s based on PM/NPS-2) is understandable. (Again, see Section 3.5.)

In the NG–N₂, NG–HNCO, and NG–CH₂O mixtures, the additive acted as a suppressant. The results for NG–N₂ were consistent with previous findings. The results for NG–CH₂O were not consistent with those published by Miller and Anderson (2000a), who found that the addition of CH₂O produced a small (1% to 7%) increase in NG(*l*)'s burning rate. As already mentioned, their result surprised them because they had thought that CH₂O would, like N₂, simply act as a diluent/heat sink and, therefore, that NG–CH₂O would burn in a manner similar to NG–N₂. But again, the mechanism that was the basis for that prediction had shortcomings that were subsequently corrected, and that result can be discounted. In this study, CH₂O had a significantly greater suppressing effect than N₂ (at 10 atm). As such, it too was at odds with Miller and Anderson's initial expectation.

As will be discussed in the sections that follow, the suppressing effect produced by CH₂O in this study appears to be attributable to its (low) $h_c^{-\infty}$ rather than kinetic activity.

3.1.2 2000 atm

Table 6 lists calculated regression rates for NG(*l*) and NG-additive mixtures burning at 2000 atm. Figure 3 presents the data graphically. Figure 3a compares (ρ_c -normalized) absolute values while Fig. 3b compares mixture regression rates relative to the rate calculated for NG(*l*) with the same mechanism/NPS model. The strong, consistent, model-dependent trends in the predictions for each mixture that were observed at 10 atm (Fig. 2) are not apparent in Fig. 3.

As shown in Table 6, the three mechanism/NPS models predicted regression rates for NG(*l*) burning at 2000 atm that were (effectively) equal to each other. However, they were 2 to 3 times higher than measured values. We note that they are also approximately 3 times higher than a calculated rate published by Miller and Anderson (2000a). However, as already discussed, the NPS specified for that calculation (3HONO+2HCO+CO) was selected from several candidates *because* it was the one that produced the burning rate in best agreement with measured values; and NG(*l*)'s burning rates were not satisfactorily reproduced when that NPS was employed with a (corrected) mechanism similar to DZ's core. Thus, one should not construe that the better agreement between calculated and measured rates obtained with the earlier model is evidence that it better represented the process than the models employed in this study.

As at 10 atm, the $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$ found necessary to sustain the productions of NPS-1 and NPS-2 at 2000 atm were significantly different (Table 7). As shown in Table 7, the surface temperatures in the simulations were approximately 1377 K. At 1377 K, the specific enthalpy of NPS-1 is 153 cal/g; NG(g)'s is 67 cal/g. Consequently, the $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$ necessary to sustain the production of NPS-1 under these conditions was 26,100 cal/cm²s while that necessary to sustain the production of NG(g) was only 22,000 cal/cm²s. Although in absolute terms the difference between the two was significantly larger than it was at 10 atm, it was less significant in relative terms. Further mediated by the difference in the reactive potentials of NPS-1 and NPS-2, the burning rates predicted by the three models ended up being the same.

Table 6 Predicted burning rates for NG(*l*) and NG-additive mixtures: 2000 atm

Mixture	<i>r</i> (cm/s)						
	Measured ^a	DZ/NPS-1		PM/NPS-1		PM/NPS-2	
		Predicted	ρ_c -normalized ^b	Predicted	ρ_c -normalized ^b	Predicted	ρ_c -normalized ^b
NG(<i>l</i>)	10–15	30	30	30	30	30	30
NG–HN ₃	...	135 [+350%]	126 [+320%]	141 [+370%]	131 [+340%]	133 [+370%]	124 [+310]
NG–N ₂ H ₄	...	57 [+90%]	56 [+87%]	57 [+90%]	56 [+87%]	51 [+70%]	50 [+67%]
NG–NH ₃	...	36 [+20%]	35 [+16%]	36 [+20%]	35 [+16%]	34 [+13%]	33 [+10%]
NG–NH ₃ –HNCO	...	32 [+7%]	31 [+3%]	32 [+7%]	31 [+3%]	32 [+7%]	31 [+3%]
NG–N ₂	...	28 [–7%]	27 [–10%]	29 [–3%]	28 [–7%]	28 [–7%]	27 [–10%]
NG–HNCO	...	29 [–3%]	28 [–7%]	30 [+0%]	29 [–3%]	30 [+0%]	29 [–3%]
NG–CH ₂ O	...	28 [–7%]	27 [–10%]	28 [–7%]	27 [–10%]	28 [–7%]	27 [–10%]
NG–urea	...	27 [–10%]	27 [–10%]	27 [–10%]	27 [–10%]	27 [–10%]	27 [–10%]
NG–urea–spv2	...	27 [–10%]	27 [–10%]	26 [–13%]	26 [–13%]	26 [–13%]	26 [–13%]

^aMiller and Anderson (2004).^b $r(\rho_c\text{-normalized}) = r(\text{predicted}) * \rho_c(\text{mixture}) / \rho_c(\text{NG}(\textit{l}))$.

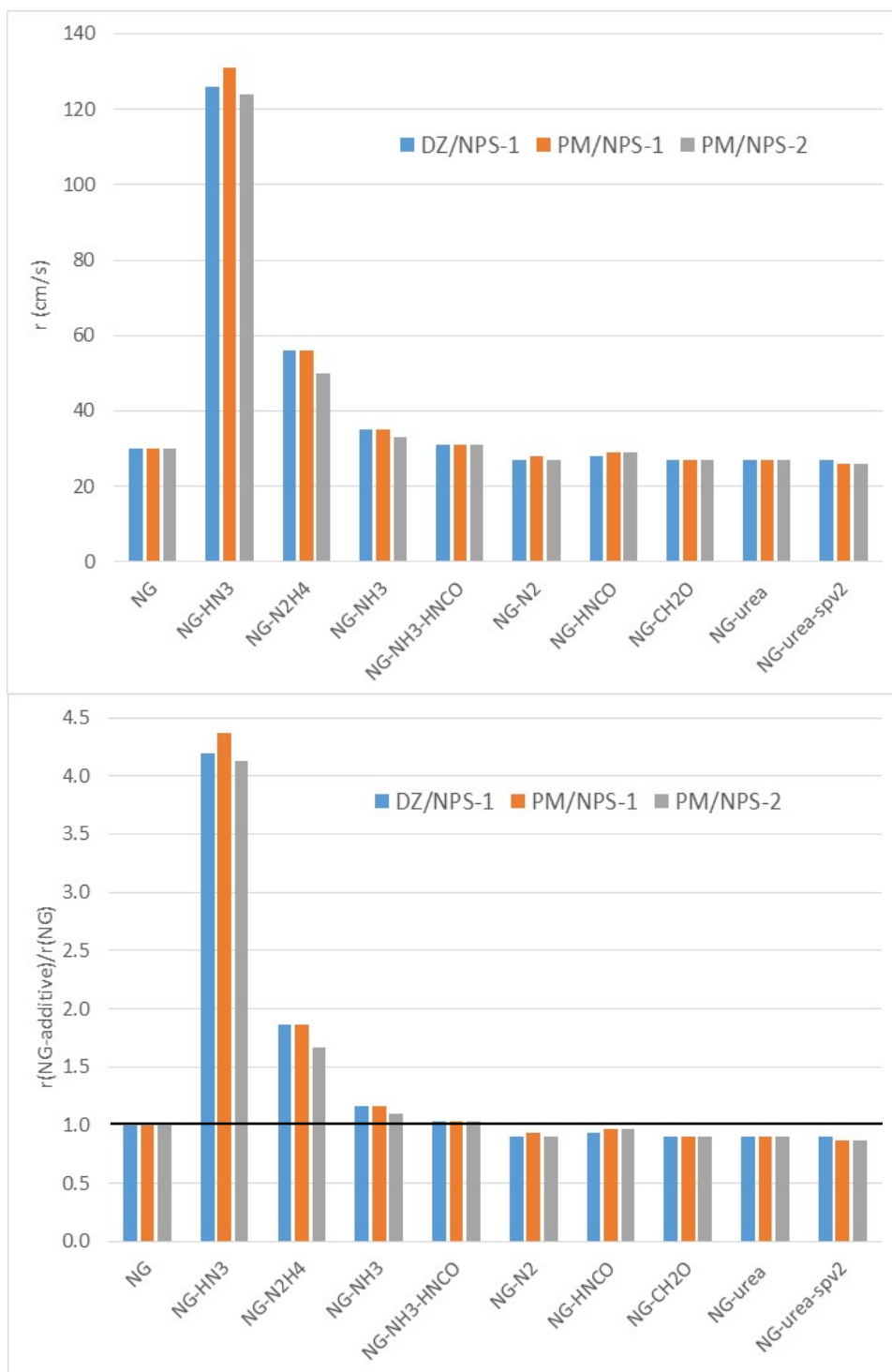


Fig. 3 Predicted regression rates (r) for NG(l) and NG-additive mixtures burning at 2000 atm: a) ρ_c -normalized absolute rates; b) rates relative to $r[NG(l)]$

Table 7 Comparisons of Eq. 1 parameters for NPS-1 and NPS-2: NG(*l*) burning at 2000 atm

NPS	r	T^0 ^c	$\sum_k^K (Y_g^k)^{-0} (h_g^k)^{+0}$	$\left[\lambda_g \frac{dT}{dx} \right]^{+0}$
	cm/s	K	cal/g	cal/cm ² s
NPS-1	15 ^a	1156	72.1	11,100
NPS-2	15 ^a	1156	-27.5	8,800
NPS-1	30 ^b	1377	153.2	26,100
NPS-2	30 ^b	1377	66.6	22,000

^aNominal measured value.

^bCalculated value.

^cCalculated based on the specified burning rate and Zenin's (1995) pyrolysis law for double-base propellants.

The impacts the additives had on NG(*l*)'s burning rate at 2000 atm were (in general) similar to those they had at 10 atm. NG–HN₃'s burning rate relative to NG(*l*)'s was larger at 2000 atm than it was at 10 atm. The relative increase produced by adding N₂H₄ was about the same at 2000 atm as it was at 10 atm. All three mechanism/NPS models' predictions for NG–NH₃'s and NG–NH₃–HNCO's burning rates were modestly higher than their predictions for NG(*l*)'s. The models' predictions for NG–HNCO's burning rate relative to NG(*l*)'s fell within a fairly narrow ($\pm 10\%$) range near 0%, indicating the addition of HNCO had little impact at this pressure. This result contrasts with the burning rate prediction for NG–HNCO at 10 atm, where HNCO produced a relatively strong suppressing effect. N₂, CH₂O, and urea acted as suppressants, but in relative terms, the rate decreases produced by their addition were not as great at 2000 atm as they were at 10 atm.

3.2 NG–Additive Flame Structures: Baseline Cases

Seeking insight into the impact each additive had on the flame structure associated with NG(*l*)'s deflagration, we plotted PREMIX's solutions for temperature and $\dot{q}$ versus distance from the surface for each baseline case. Results for NG(*l*) burning at 10 atm are shown in Fig. 4. All three models produced temperature profiles that reflected the two-stage structure of flames produced by nitrate esters (and nitramines) burning at low pressures. (Given DZ/NPS-1's and PM/NPS-1's origins, this was expected from them. The results produced by PM/NPS-2 were gratifying.)

Near the surface, which was the region of most interest in this study, the $\dot{q}$ versus distance plot produced by PM/NPS-2 was distinctly different from those produced by DZ/NPS-1 and PM/NPS-1. In the latter two, $\dot{q}$ values exceeded 3×10^7 cal/cm³s at the surface and quickly fell to less than 1×10^5 cal/cm³s within

3 μm of the surface before peaking again at approximately 10 μm . The maximum of the second feature was approximately $6 \times 10^5 \text{ cal/cm}^3\text{s}$. The $\dot{q}$ versus distance plot produced by PM/NPS-2 rose from less than $1 \times 10^5 \text{ cal/cm}^3\text{s}$ at the surface to a maximum of approximately $1 \times 10^6 \text{ cal/cm}^3\text{s}$ at approximately 4 μm from the surface before declining.

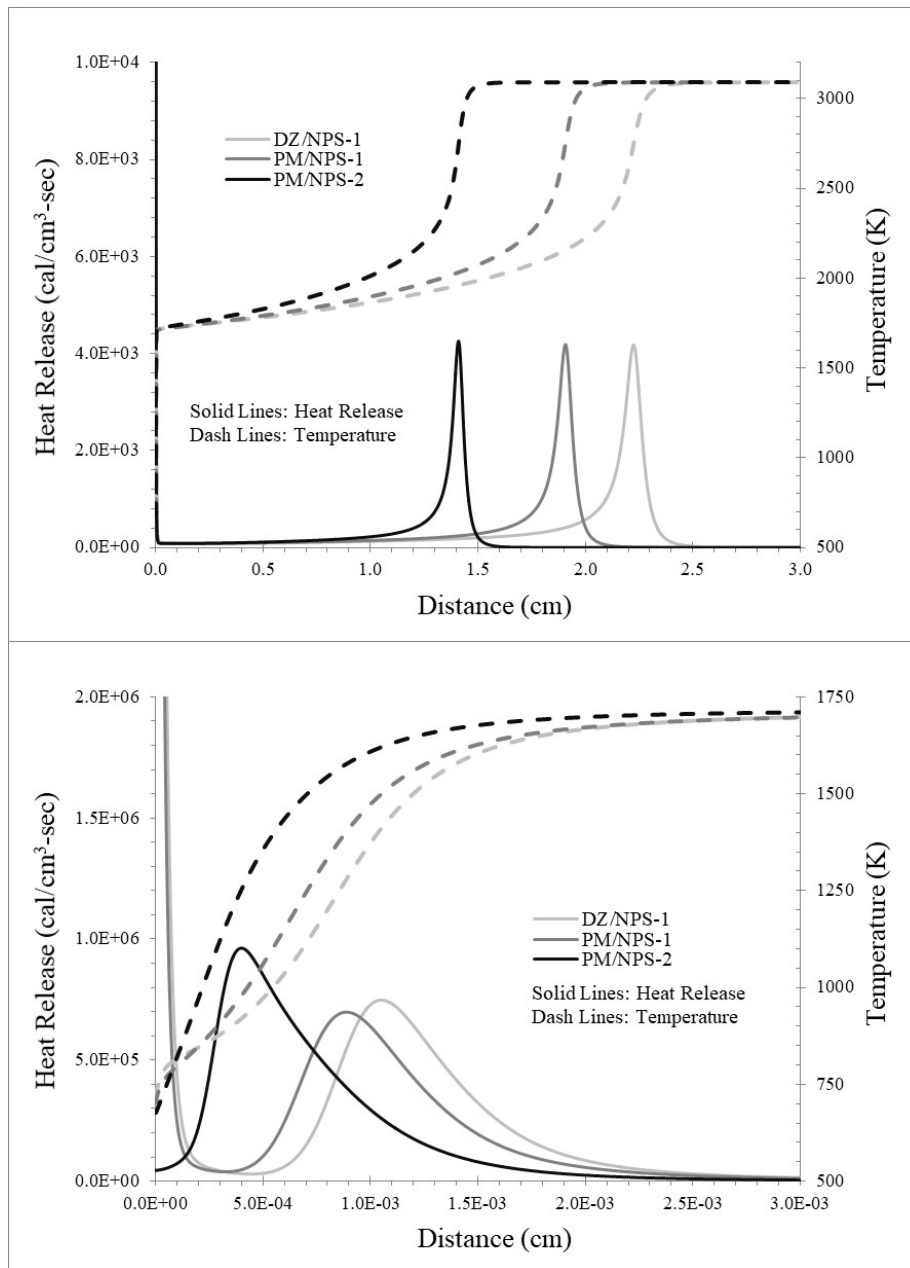


Fig. 4 Computed temperature and heat release vs. distance plots for NG(l) burning at 10 atm

As will be discussed in Section 3.3, at 10 atm the reaction most responsible for the large temperature rise adjacent to the surface was $\text{HCO} + \text{NO}_2 = \text{H} + \text{CO}_2 + \text{NO}$ (R351). And as already discussed, the concentrations of HCO and NO_2 specified in NPS-1 were considered likely to create unrealistically high concentrations of these species adjacent to the surface. Nonetheless, the $\dot{q}$ produced by PM/NPS-2 led to higher temperatures at distances from 1 to 30 μm from the surface and a shorter d_{DZ} than those produced by DZ/NPS-1 and PM/NPS-1. At the same time, indicating the similarity of the solutions, the τ_{DZ} for the three cases were almost identical: $\tau_{DZ}(\text{DZ/NPS-1}) = 2.21 \text{ ms}$; $\tau_{DZ}(\text{PM/NPS-1}) = 2.23 \text{ ms}$; $\tau_{DZ}(\text{PM/NPS-2}) = 2.19 \text{ ms}$. This can be rationalized by noting that in each of the simulations the temperature at the completion of the first-stage was approximately 1700 K, suggesting that in each case the chemical compositions were almost identical at this point as well.

Seeking an explanation for this (initially) surprising result, we plotted cumulative $\dot{q}s$ as a function of distance from the surface for the three cases. That revealed a difference between the PM/NPS-2-based solution and those generated by DZ/NPS-1 and PM/NPS-1 that was not apparent from consideration of Fig. 4 alone. That is, much less heat was released (per unit distance) in PM/NPS-2's solution than in the other two. Observing also that all three simulations had the same $h_c^{-\infty}$ and (effectively) the same ending specific enthalpy, with the latter conclusion inferred from the similarity of the final temperatures, the differences in the cumulative values were clearly due to the differences in the burning rates (or $\dot{m}$) (see Table 4).

Exposing the codependence of $\dot{q}$ and $\dot{m}$, the observation prompted us to consider the models' energy equation (Kee et al. 1985), which may be written,

$$\frac{dT}{dx} = \frac{\dot{q} - \frac{d}{dx} \left(\lambda_g \frac{dT}{dx} \right)}{\dot{m} c_{p,g} + \sum_{k=1}^K \rho_g V_g^k V_g^k c_{p,g}^k}, \quad (12)$$

where $c_{p,g}$ is the (x -dependent) heat capacity of the gas (mixture), ρ_g is its density, and V_g^k and $c_{p,g}^k$ are, respectively, the diffusion velocities and heat capacities of individual species. Informed in this manner, the higher temperatures of the first stage of the PM/NPS-2 simulation can certainly be rationalized: (other things being equal) the temperature gradient is inversely proportional to $\dot{m}$ (or r), and, therefore, lower $\dot{m}$'s have the potential to produce higher first-stage temperatures. This, in turn, can lead to a greater fraction of the stored chemical energy per gram of NG(l) being converted to kinetic energy prior to the onset of the second heat release feature. And, given that, one would expect d_{DZ} to be shorter. Indeed, this relationship between d_{DZ} and $\dot{m}$ was also observed in the results produced by DZ/NPS-1 and PM/NPS-1 (see Fig. 4 and Table 4).

As a final observation concerning this matter, we note that our (faulty) expectation that a lower burning rate would correspond to a longer d_{DZ} had precedence. For one, this correlation was observed when comparing results for NG(*l*) with results for NG–NH₃ and NG–N₂ (Miller and Anderson 2000a). Moreover, as mentioned in the introduction, Miller and Anderson found that reactions that were important determinants of nitrate-ester d_{DZ} s were also important determinants of nitrate-ester burning rates. But as also mentioned, they deduced that correlation on the basis of results produced for systems burning at different pressures. In addition, we failed to properly weigh “exceptions”, such as results for NG–HNCO (Miller and Anderson 2000b). Per Eq. 12, if anything, when comparing similar systems burning at the same pressure, lower burning rates will correspond to shorter d_{DZ} s. But as the examples informing our initial expectation and other results presented in this report make clear, that correlation is not reliable. The interplay between all the factors with the potential to influence both the burning rate and d_{DZ} , including but not limited to $h_c^{-\infty}$ and the (*x*-dependent) $c_{p,g}$ and ρ_g of the gas, is complex, limiting the import of simple correlations and, specifically, compromising d_{DZ} ’s usefulness as a standalone indicator of kinetic activity with the potential to impact a burning rate.

Results from the three models’ solutions for NG(*l*) burning at 2000 atm are shown in Fig. 5. Close to the surface, the results produced by the models were analogous to the ones they produced at 10 atm, but compressed. Indeed, in all the solutions the first stage of combustion was almost complete within 0.2 μm (200 nm) of the surface. Also, as at 10 atm, the plots suggested a two-stage flame structure, with the onset of the second stage occurring in this case approximately 1–2 μm from the surface. (As such, the dark zone would not be observable to the naked eye.) And again, the first-stage temperatures predicted by PM/NPS-2 were larger than those predicted by PM/NPS-1 and DZ/NPS-1, and PM/NPS-2 predicted a d_{DZ} that was shorter than those predicted by PM/NPS-1 and DZ/NPS-1.

Except for NG–HN₃, the characteristics of the temperature and $\dot{q}$ versus distance plots produced by the three models for the NG–additive mixtures were qualitatively similar to those produced for NG(*l*), and the trends they predicted were similar as well. Therefore, to condense the discussion, except for a couple of instances, we will restrict it to comparing results produced by PM/NPS-2.

Figures 6 and 7 present temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2’s solutions for NG–HN₃ burning at 10 and 2000 atm, respectively. As shown in Fig. 6, there was no evidence of two stages in the flame at 10 atm. The vast majority of the stored chemical energy was released within 0.002 cm (20 μm) of the surface, and the temperature rose above 2500 K within that distance.

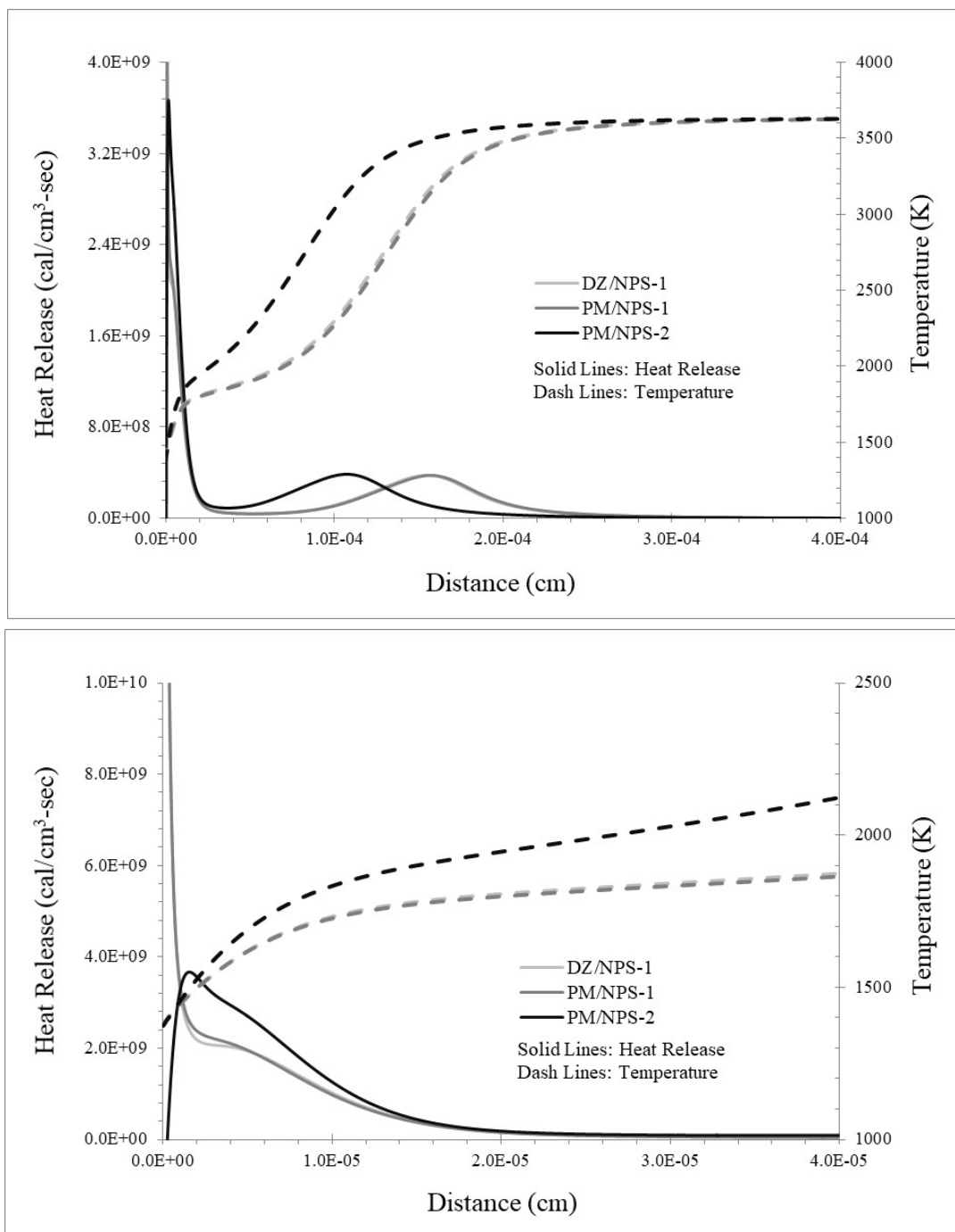


Fig. 5 Computed temperature and heat release vs. distance plots for NG(l) burning at 2000 atm

At 2000 atm, there was a slight shoulder on the main $\dot{q}$ feature, and the temperature profile exhibited some structure. However, given the overwhelming differences between the solutions for NG–HN₃ and NG(*l*), we did not believe knowledge of the mechanism underlying the structure would warrant the effort needed to obtain it. Therefore, no attempt was made.

Figure 8 presents temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solution for NG–N₂H₄ burning at 10 atm. In this case, the d_{DZ} in the solution for NG–N₂H₄ was considerably shorter than it was in the solution for NG(*l*): approximately 0.4 cm versus approximately 1.4 cm. Near the surface, considerably more heat was released by NG–N₂H₄, and the temperature gradient was larger. By 0.001 cm (10 μ m) the temperature of the solution for NG–N₂H₄ was more than 300 K higher than the corresponding result for NG(*l*).

As shown in Fig. 9, at 2000 atm the added N₂H₄ also led to considerably more heat being released near the surface and higher first-stage temperatures. Given only that, we would have guessed that $d_{DZ}(\text{NG–N}_2\text{H}_4)$ would have been shorter than $d_{DZ}(\text{NG}(\textit{l}))$, but it was not: 1.7 μ m versus 1.1 μ m. An explanation for this surprising result is proffered in Section 3.3.

Figure 10 presents temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solution for NG–NH₃ burning at 10 atm. The changes in the magnitudes and locations of the main features of the $\dot{q}$ traces are analogous to those observed for NG–N₂H₄, albeit not as dramatic. However, there was a small shoulder on the $\dot{q}$ feature near the surface that was not observed in the solution for NG(*l*). Being approximately 3 orders of magnitude smaller than the main feature, we did not initially consider it likely that the (sub)mechanism responsible for it would also influence the system's burning rate. Nonetheless, we examined details of the chemistry in the region of the shoulder, and found that the major source of $\dot{q}$ was $\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$ (R148), and that the major source of NH_2 was $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$ (R149). This was intriguing because, despite the subsequently identified and corrected shortcomings of the mechanism/NPS model employed by Miller and Anderson (2000a) in their first study of this system, it predicted a higher burning rate for NG–NH₃ than NG(*l*), and these two reactions were identified as the (sub)mechanism responsible for the higher rate. But as discussed in the introduction, Conner et al. (2008) reported that a model similar to DZ/NPS-1 found that the addition of NH₃ had little impact on the burning rate of NC. And as shown in Table 4, DZ/NPS-1 found that the addition of NH₃ had little impact on NG(*l*)'s burning rate.

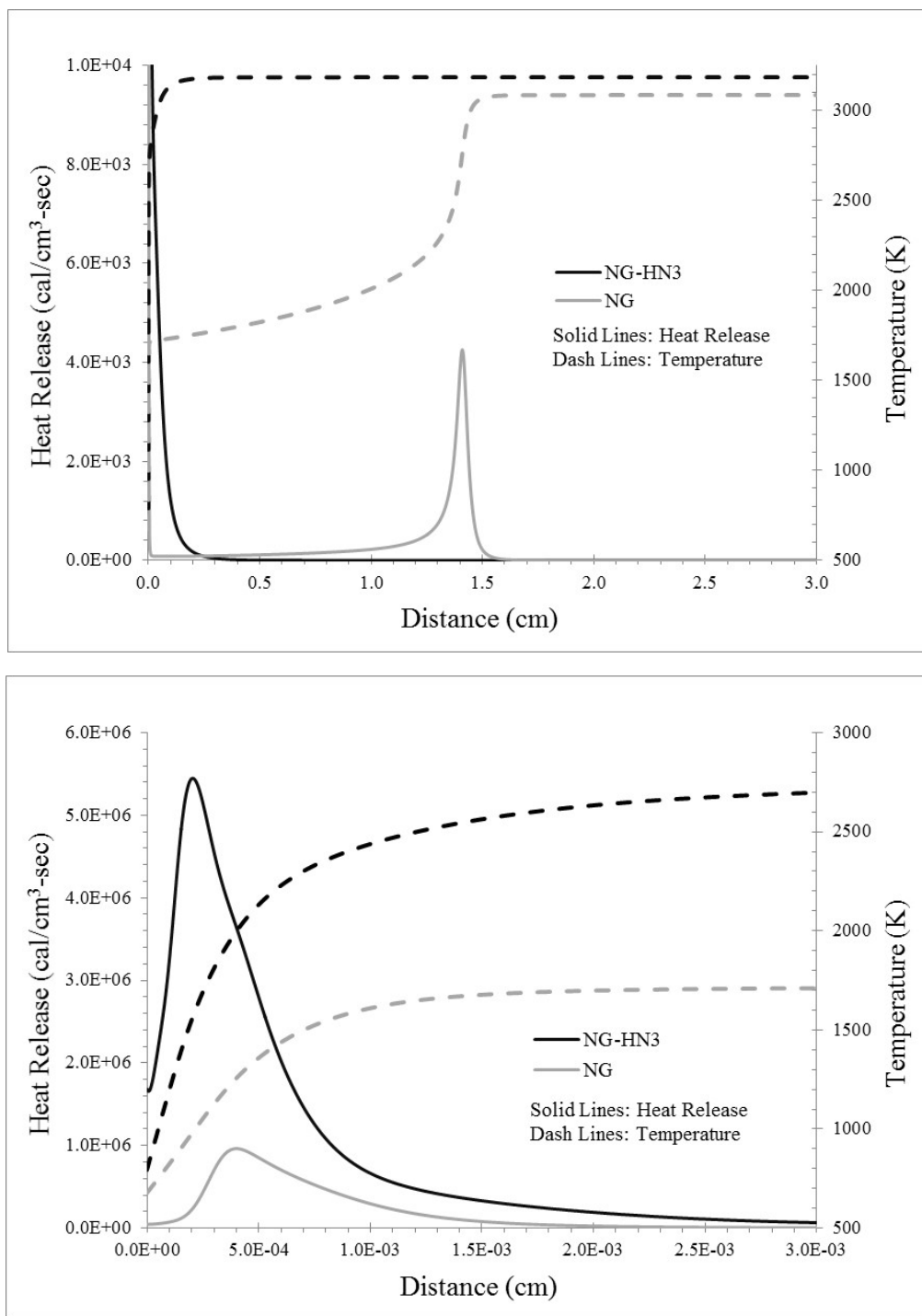


Fig. 6 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-HN₃ burning at 10 atm

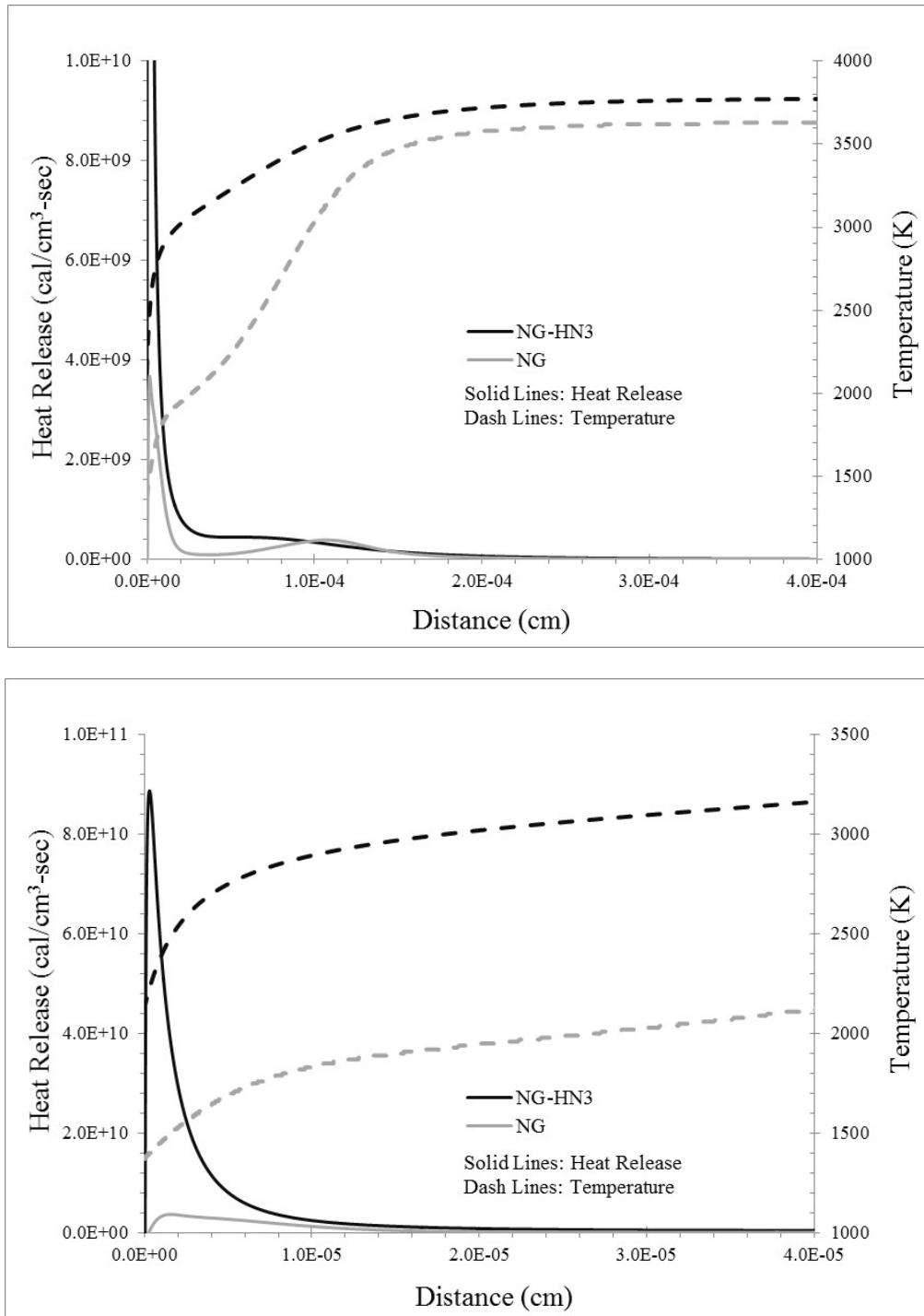


Fig. 7 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-HN₃ burning at 2000 atm

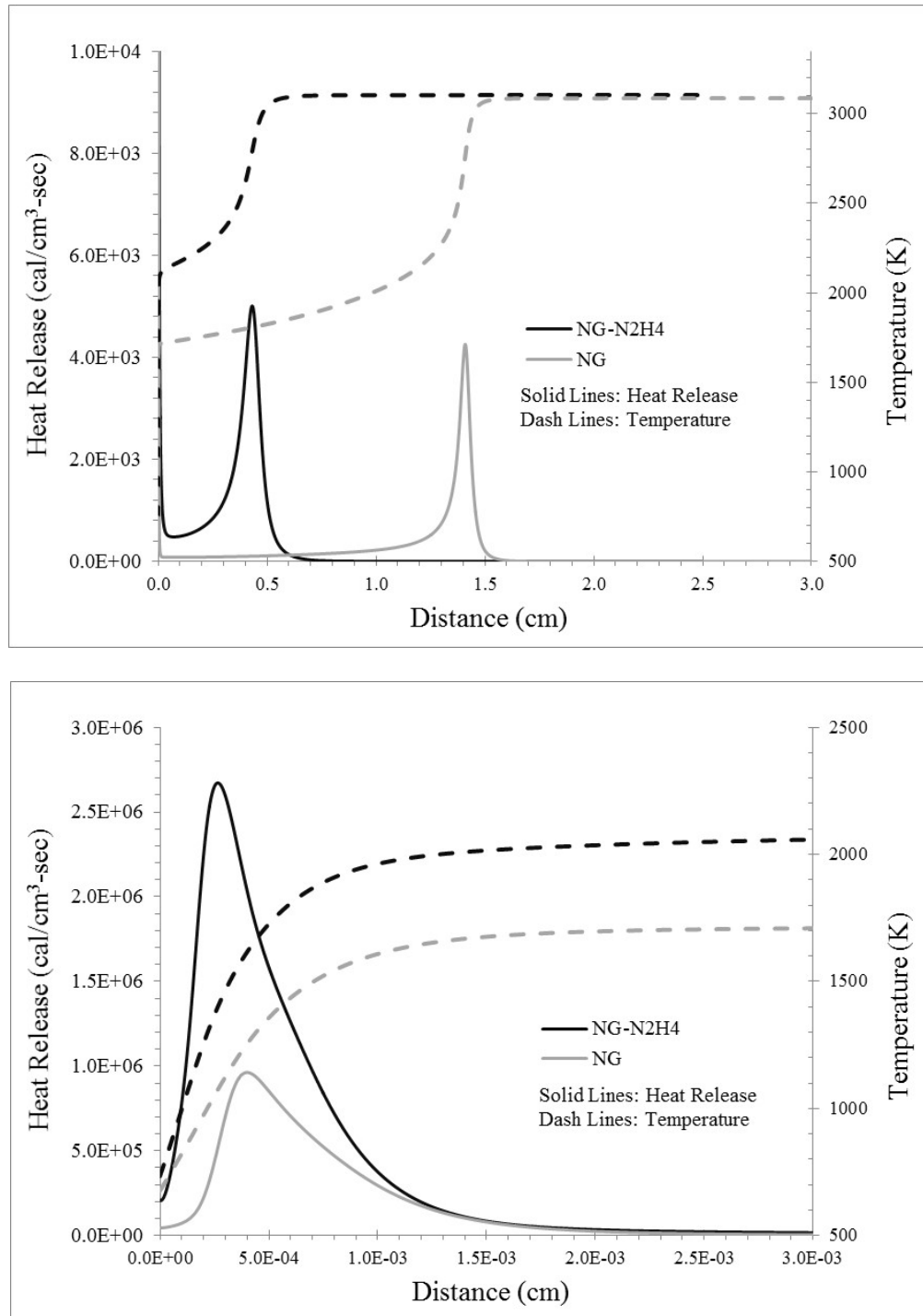


Fig. 8 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-N₂H₄ burning at 10 atm

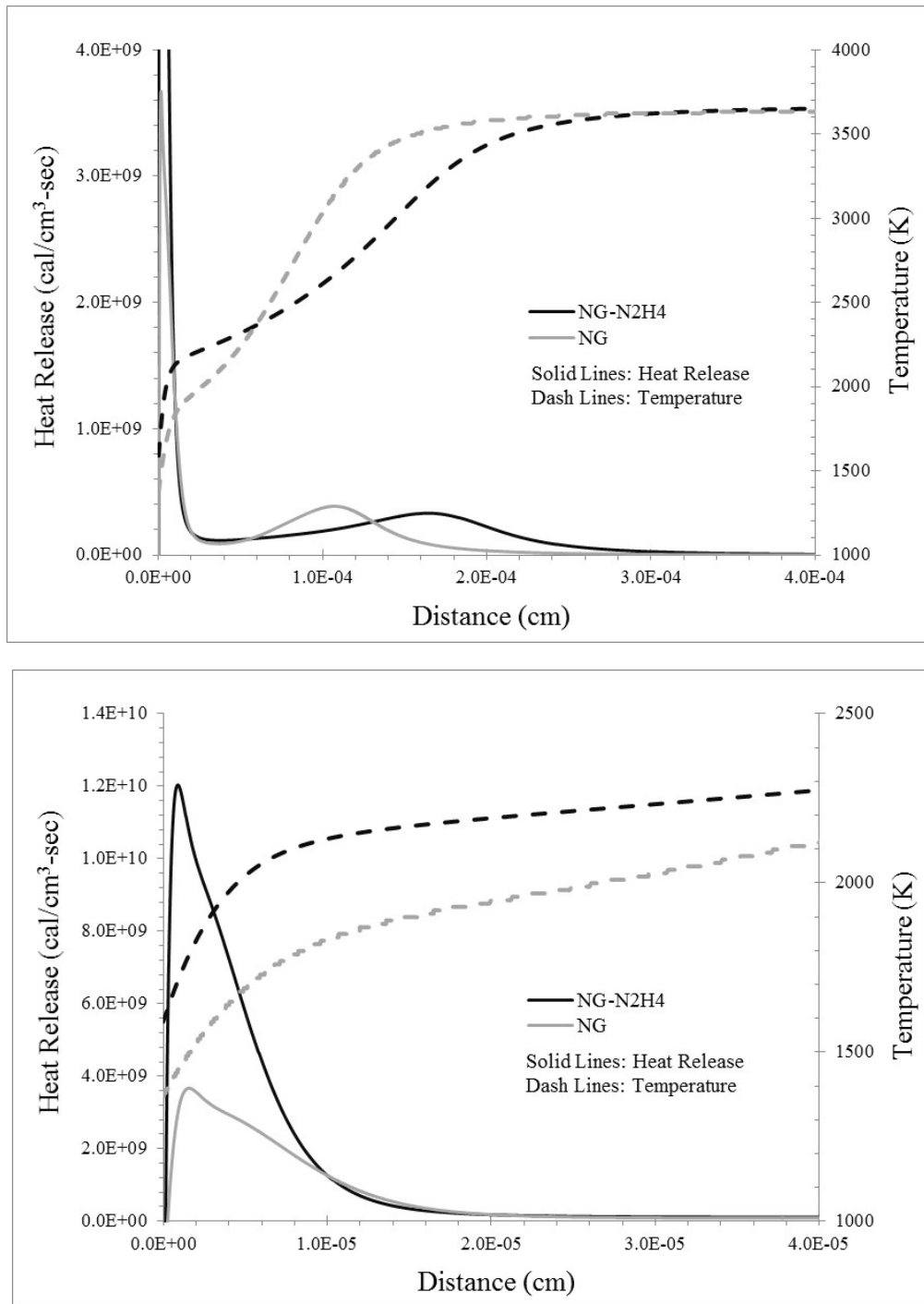


Fig. 9 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-N₂H₄ burning at 2000 atm

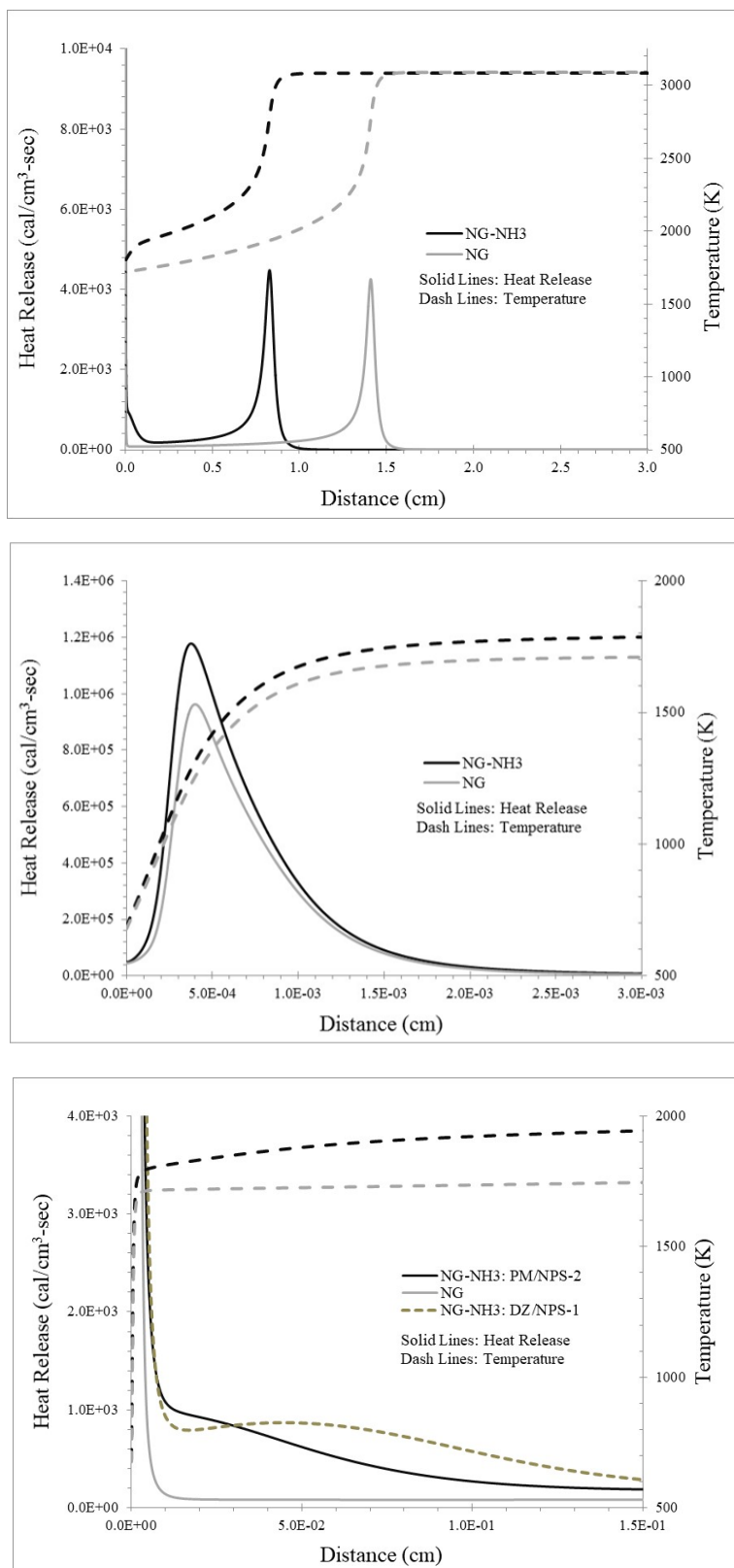


Fig. 10 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-NH₃ burning at 10 atm

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Seeking to understand the differences between the models that led to the different predictions for NH_3 's impact on $\text{NG}(l)$'s burning rate, we compared the $\dot{q}$ versus distance trace produced by DZ/NPS-1 with that produced by PM/NPS-2. Shown in the lowest panel of Fig. 10, the comparison suggested there was a mismatch between the transit times/length scales of the primary mechanism driving deflagration and the NH_3 -induced (sub)mechanism underlying the shoulder that limited the (sub)mechanism's potential to augment $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$, and when modeled with DZ/NPS-1, the mismatch was greater. Sensitivity analyses corroborating this conclusion are presented and discussed in Section 3.3.

Figure 11 presents temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solution for NG-NH_3 burning at 2000 atm. Unlike the results produced for this mixture burning at 10 atm, where the addition of NH_3 produced a prominent shoulder on the primary $\dot{q}$ feature, except for the slight difference in their magnitude, differences between the $\dot{q}$ traces near the surface of the NG-NH_3 and $\text{NG}(l)$ systems were unremarkable. As was found in comparing $d_{DZ}(\text{NG-N}_2\text{H}_4)$ to $d_{DZ}(\text{NG}(l))$, $d_{DZ}(\text{NG-NH}_3)$ was longer than $d_{DZ}(\text{NG}(l))$. But the difference was not nearly as large and was not further investigated.

Figures 12 and 13 present temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solutions for NG-N_2 burning at 10 and 2000 atm, respectively. As found by Miller and Anderson (2000a), N_2 's addition decreased $\dot{q}$ and lengthened d_{DZ} .

Figures 14 and 15 present temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solutions for NG-HNCO burning at 10 and 2000 atm, respectively. At 10 atm, $d_{DZ}(\text{NG-HNCO})$ was significantly shorter than $d_{DZ}(\text{NG}(l))$. A similar result was previously reported by Miller and Anderson (2000b). We also note that, like the $\dot{q}$ trace produced for NG-NH_3 burning at 10 atm, there was a shoulder on the $\dot{q}$ feature near the surface in the trace produced for NG-HNCO burning at 10 atm. However, it peaked at a farther distance from the surface: approximately 0.09 cm versus <0.05 cm. To determine if there were different mechanisms underlying the creation of this feature in the NG-NH_3 and NG-HNCO systems, details of the chemistry in the interval were examined. They indicated that in both cases, $\text{NH}_2+\text{NO}=\text{N}_2+\text{H}_2\text{O}$ (R148) was the major source of $\dot{q}$. However, in the NG-HNCO simulation, the primary source of NH_2 was $\text{HNCO}+\text{H}=\text{NH}_2+\text{CO}$ (R181), not $\text{NH}_3+\text{OH}=\text{NH}_2+\text{H}_2\text{O}$ (R149). As will be discussed in Section 3.3, this was also the case at the 2nd grid point.

Figures 16 and 17 present temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solutions for NG-CH₂O burning at 10 and 2000 atm, respectively. We again note that Miller and Anderson (2000a) had not expected CH₂O to be kinetically active and, therefore, that NG-CH₂O would burn like NG-N₂. However, their model predicted NG-CH₂O would burn at the about the same rate as NG(*l*), not slower. In this study, all the models predicted $r(\text{NG-CH}_2\text{O})$ would be fairly significantly less than $r(\text{NG-N}_2)$ at 10 atm, and they also predicted $r(\text{NG-N}_2)$ would be fairly significantly less than $r(\text{NG}(\textit{l}))$. Differences between the plots presented in Figs. 16 and 12 indicate the greater suppressing effect CH₂O had on $\dot{q}$ near the surface. In the NG-CH₂O system, the first $\dot{q}$ feature peaked at approximately 6.0×10^{-5} cal/cm³s while in the NG-N₂ system it peaked at approximately 7.6×10^{-5} cal/cm³s. At 2000 atm, however, PM/NPS-2's results for the two systems were consistent with Miller and Anderson's initial speculation. The $\dot{q}$ versus distance plots produced for the two systems were very similar (compare Fig. 17 to Fig. 13) and $r(\text{NG-CH}_2\text{O})$ was approximately equal to $r(\text{NG-N}_2)$.

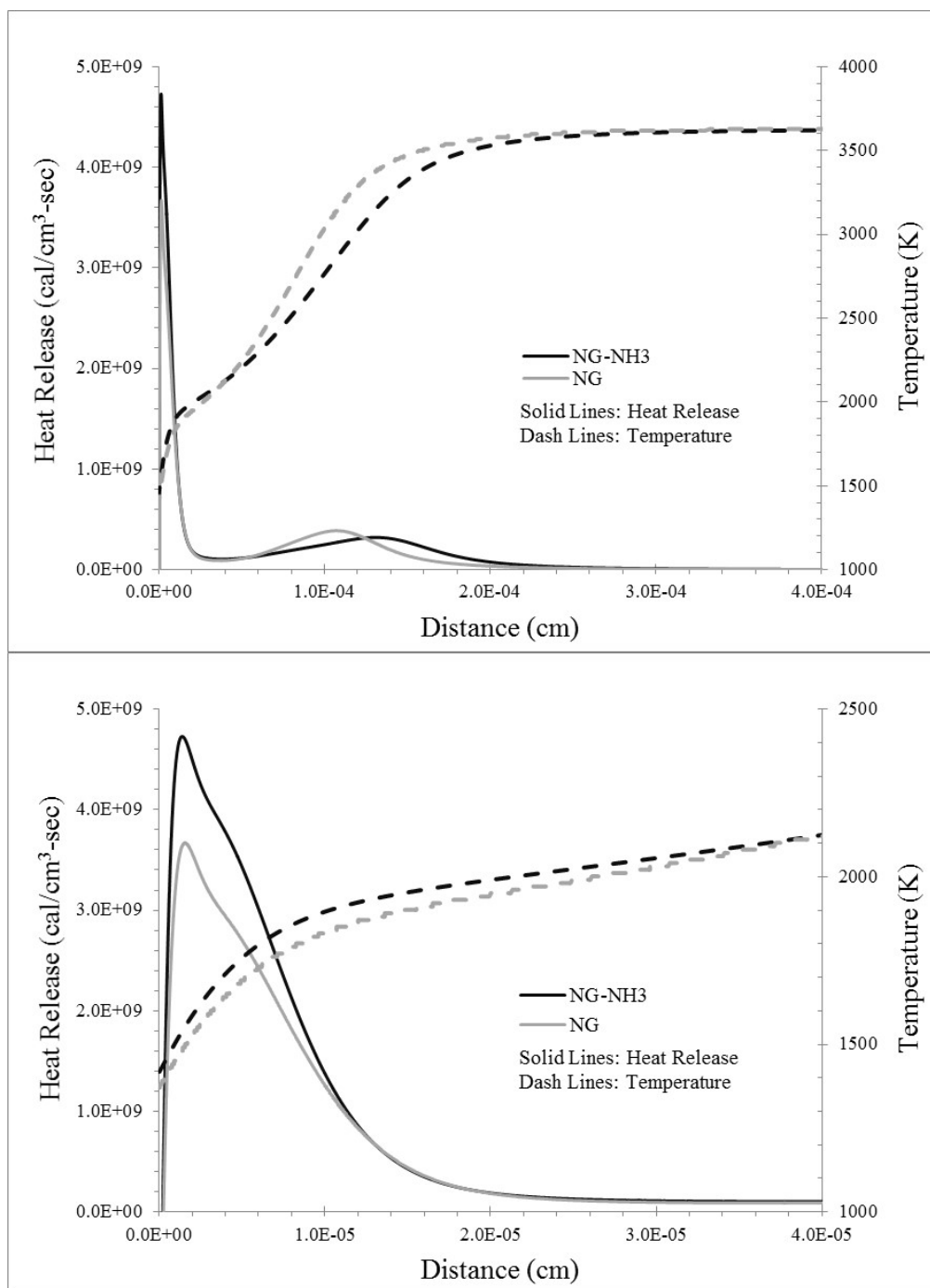


Fig. 11 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-NH₃ burning at 2000 atm

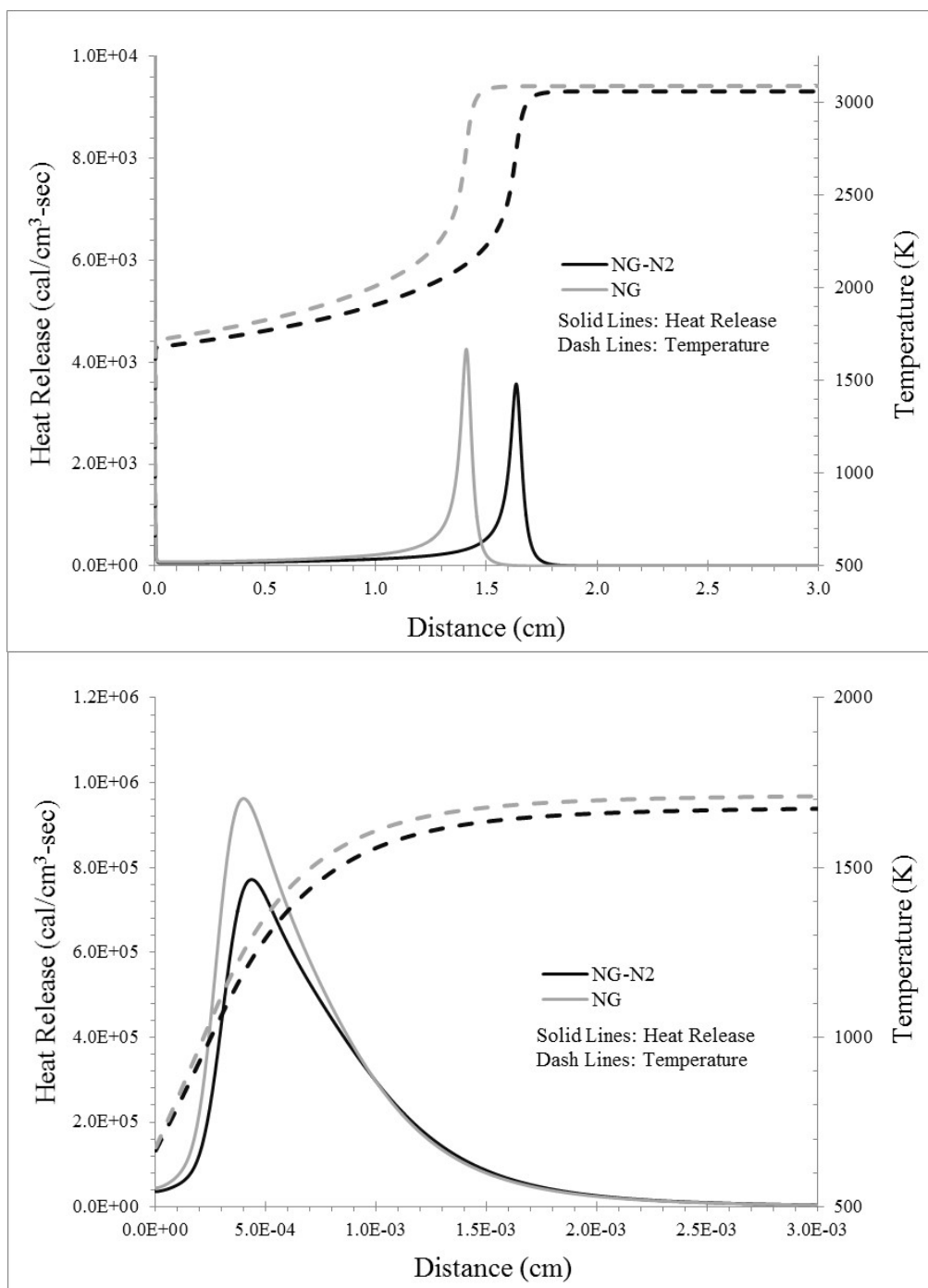


Fig. 12 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-N₂ burning at 10 atm

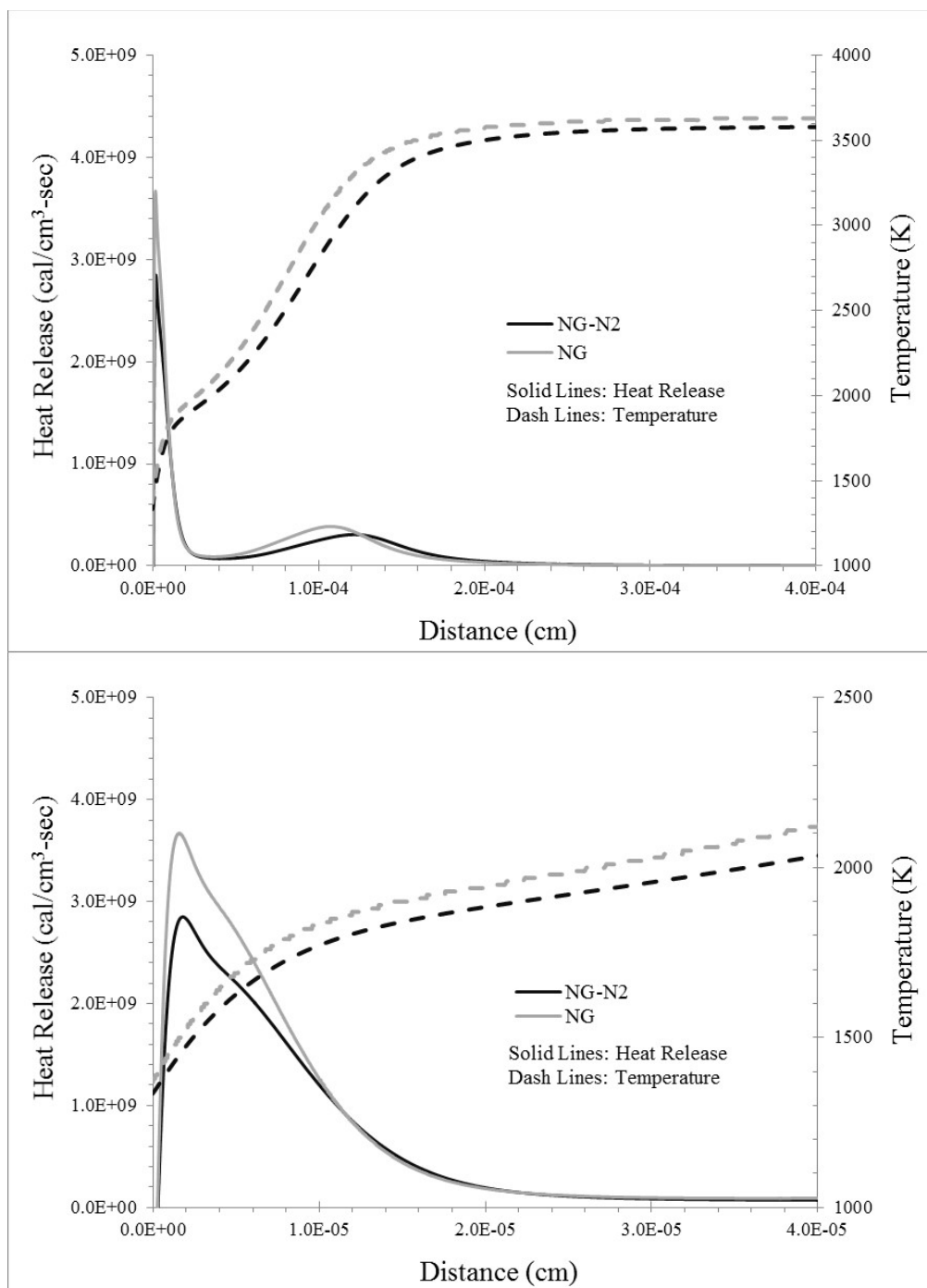


Fig. 13 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-N₂ burning at 2000 atm

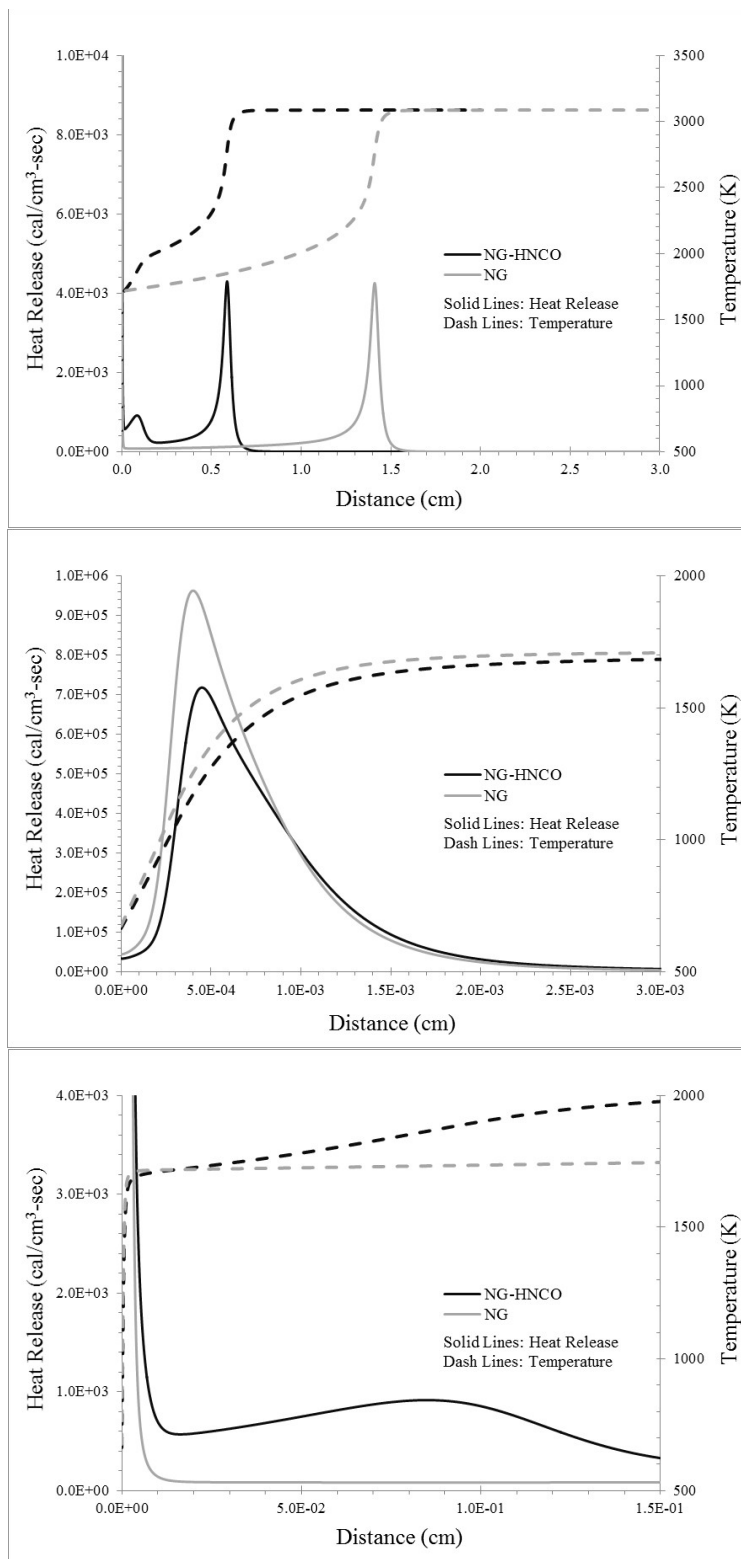


Fig. 14 PM/NPS-2 computed temperature and heat release vs. distance plots for NG–HNCO burning at 10 atm

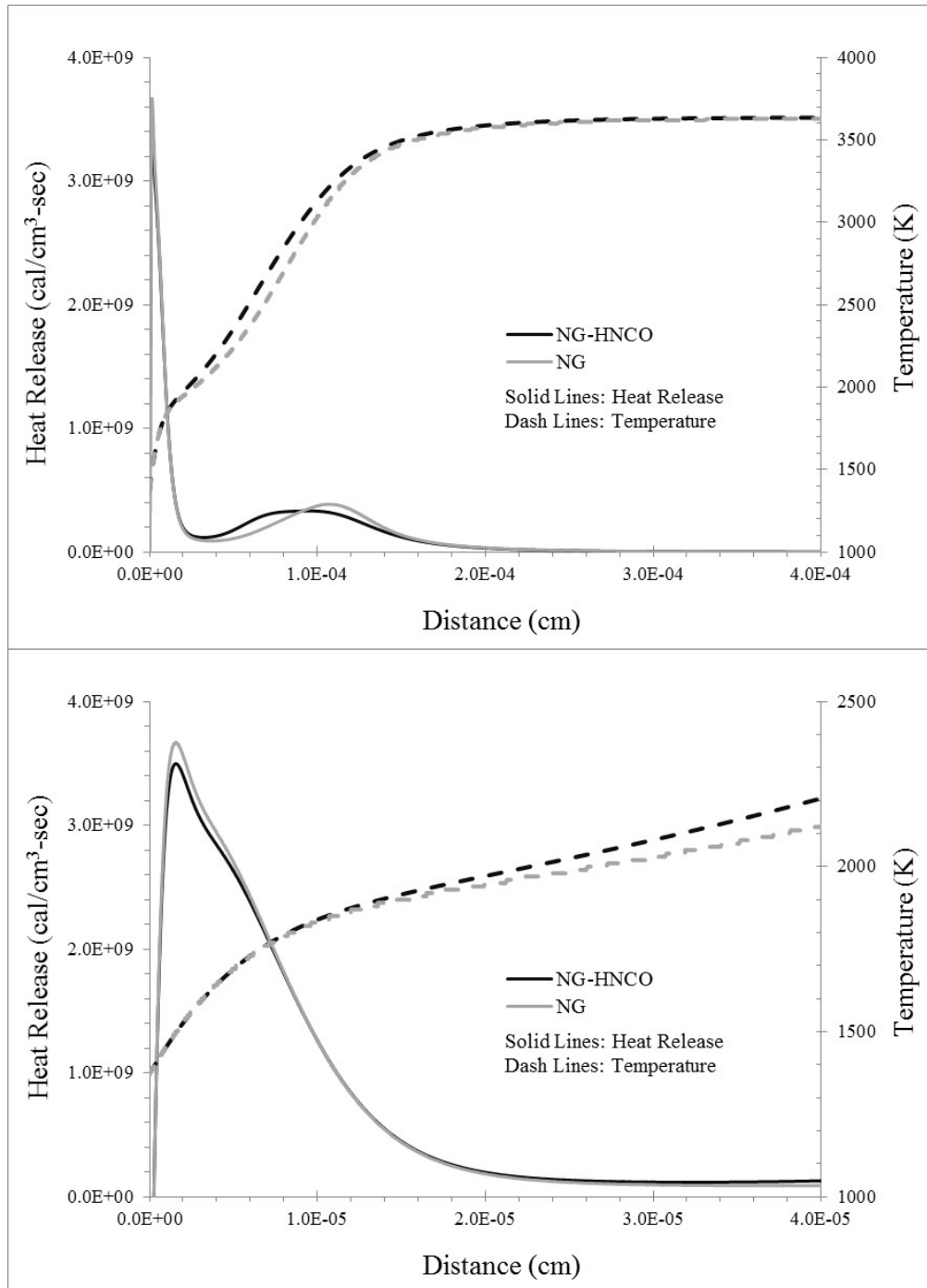


Fig. 15 PM/NPS-2 computed temperature and heat release vs. distance plots for NG–HNCO burning at 2000 atm

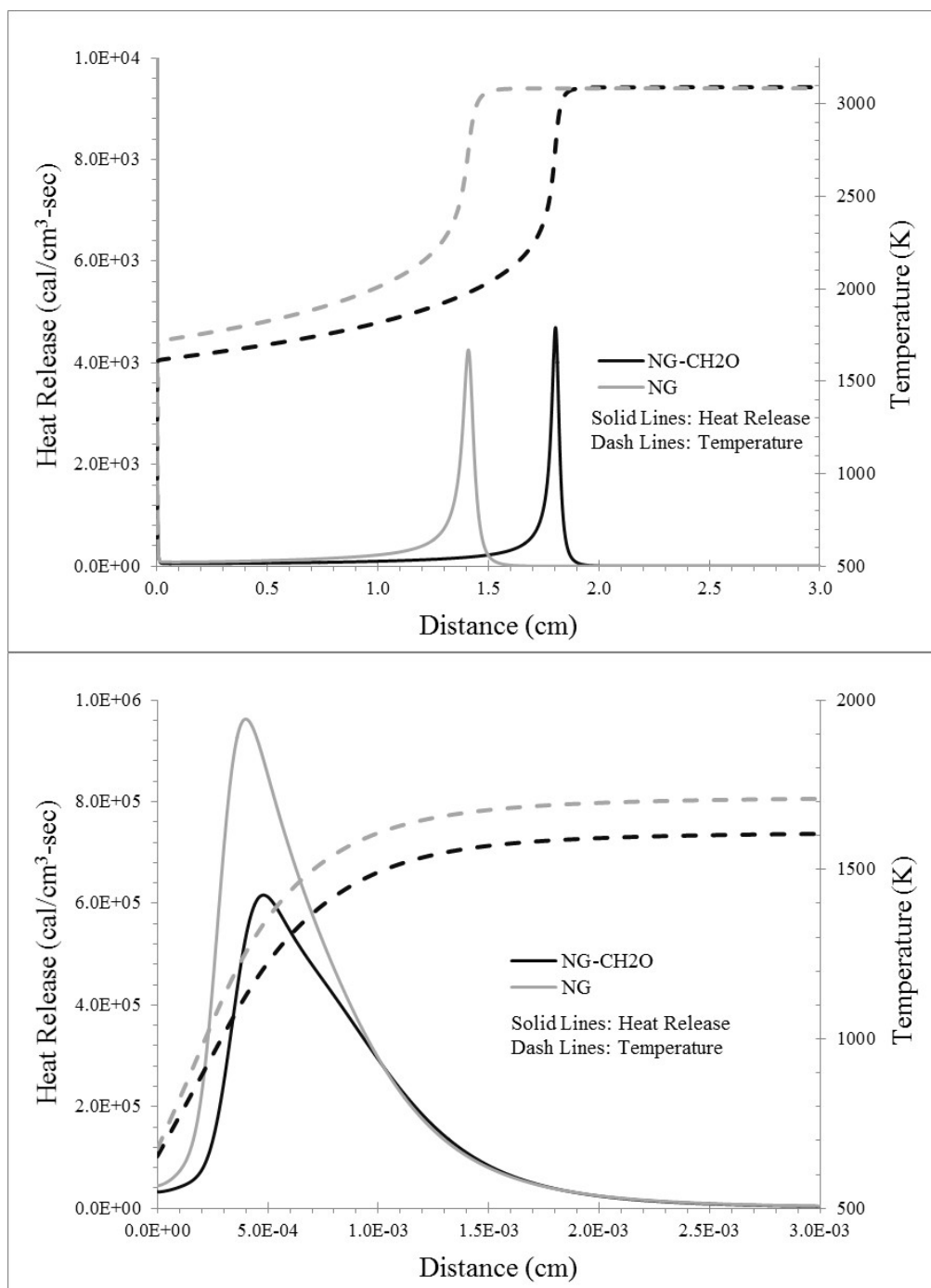


Fig. 16 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-CH₂O burning at 10 atm

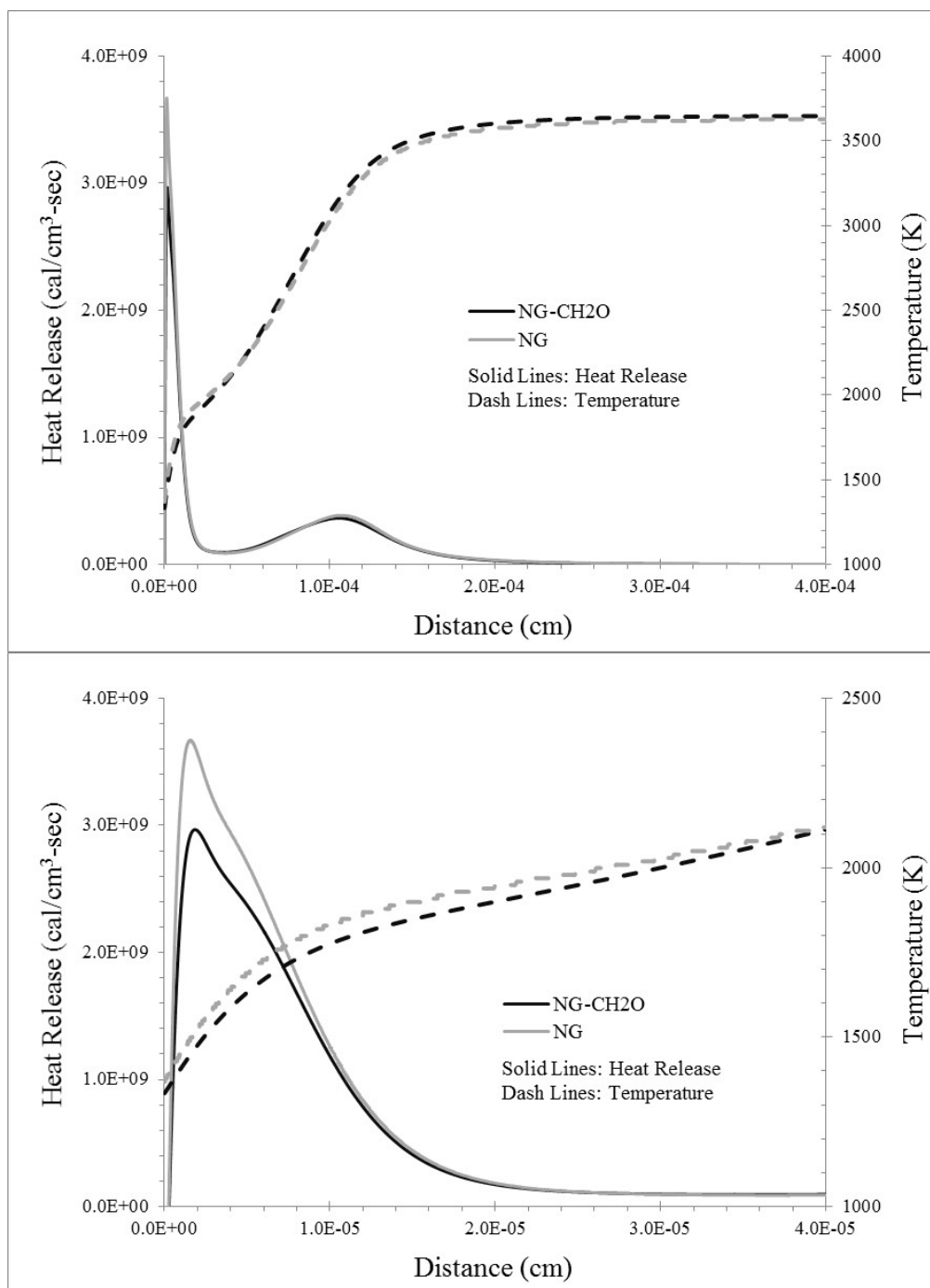


Fig. 17 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-CH₂O burning at 2000 atm

Figures 18 and 19 present temperature and $\dot{q}$ versus distance plots obtained from PM/NPS-2's solutions for NG-urea burning at 10 and 2000 atm, respectively. At 10 atm, the shoulder on the $\dot{q}$ feature adjacent to the surface that was observed in the $\dot{q}$ traces for NG-NH₃ and NG-HNCO was again observed. In those cases, the shoulder appeared to be associated with a mechanism with the potential to augment

$\left[\lambda_g \frac{dT}{dx}\right]^{+0}$. However, the magnitude of the first $\dot{q}$ feature in the solution for NG-urea was greatly reduced, and NG-urea's burning rate was the lowest of all the mixtures investigated. As discussed in Section 3.5, this result appears to be attributable to the mixture's low $h_c^{-\infty}$. At 2000 atm, the differences between the plots for the NG-urea and NG(*l*) systems were not quite as great, and on a relative basis, the difference in their burning rates was smaller.

Figures 20 and 21 compare $\dot{q}$ versus distance plots obtained from PM/NPS-2's solutions for NG-urea, NG-urea-spv2, and NG-NH₃-HNCO burning at 10 and 2000 atm, respectively. As previously mentioned, the (global) stoichiometries of these mixtures were the same. The only difference between the calculations for NG-urea and NG-urea-spv2 was the specification of their NPSs: gaseous urea and NH₃+HNCO, respectively. As shown in the lower panel of each figure, near the surface NG-urea's $\dot{q}$ trace was slightly above NG-urea-spv2's, and as one would expect on the basis of these results, NG-urea's burning rates were slightly higher than NG-urea-spv2's. (See Tables 4 and 6.) Immediately producing species with the potential to accelerate the conversion of NO to N₂, one might have thought that the opposite would occur. However, as we noted in Section 3.1, it is not just the reactive potential of the ingredient's nascent products that is important. The energy needed to convert a unit mass of an ingredient into those products is important as well.

A comparison of the $\dot{q}$ traces obtained from the solutions for NG-urea-spv2 and NG-NH₃-HNCO was also instructive. The only difference between the calculations that produced them was the specification for $h_c^{-\infty}$: -434 cal/g and -405 cal/g, respectively. As shown in the lower panel of each figure, near the surface NG-NH₃-HNCO's $\dot{q}$ traces were significantly above NG-urea-spv2's, and as one would expect on that basis, NH₃-HNCO's burning rates were significantly higher than NG-urea-spv2's. (Again, see Tables 4 and 6.) As such, these results demonstrate that the relationship between changes in $h_c^{-\infty}$ and changes in r is not as simple as one might guess on the basis of Eq. 1 (and assuming $\left[\lambda_g \frac{dT}{dx}\right]^{+0}$ was nearly the same for the two cases). Rather, the difference in $h_c^{-\infty}$ produced differences in $\dot{q}$ (and dT/dx) that were consistent with changes one would expect to obtain by changing $T^{-\infty}$. We also note that these results demonstrate that a change in $\dot{q}$ due to a change in $h_c^{-\infty}$ (or $T^{-\infty}$) is not readily distinguishable from a change in $\dot{q}$ due to kinetic activity. Therefore, one needs to perform more fundamental analyses to attribute changes in $\dot{q}$ (and r) to one factor or the other when both are relevant.

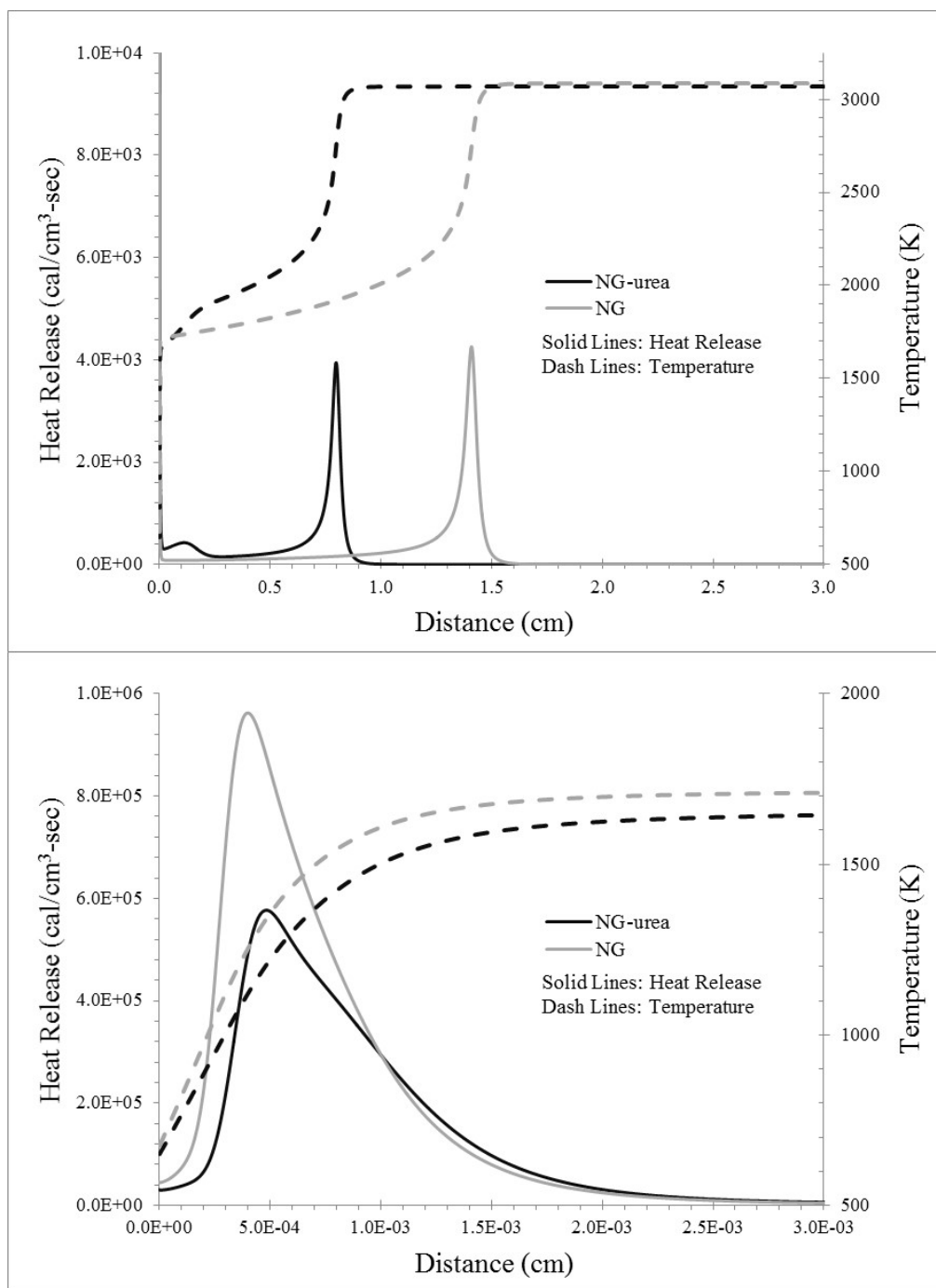


Fig. 18 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-urea burning at 10 atm

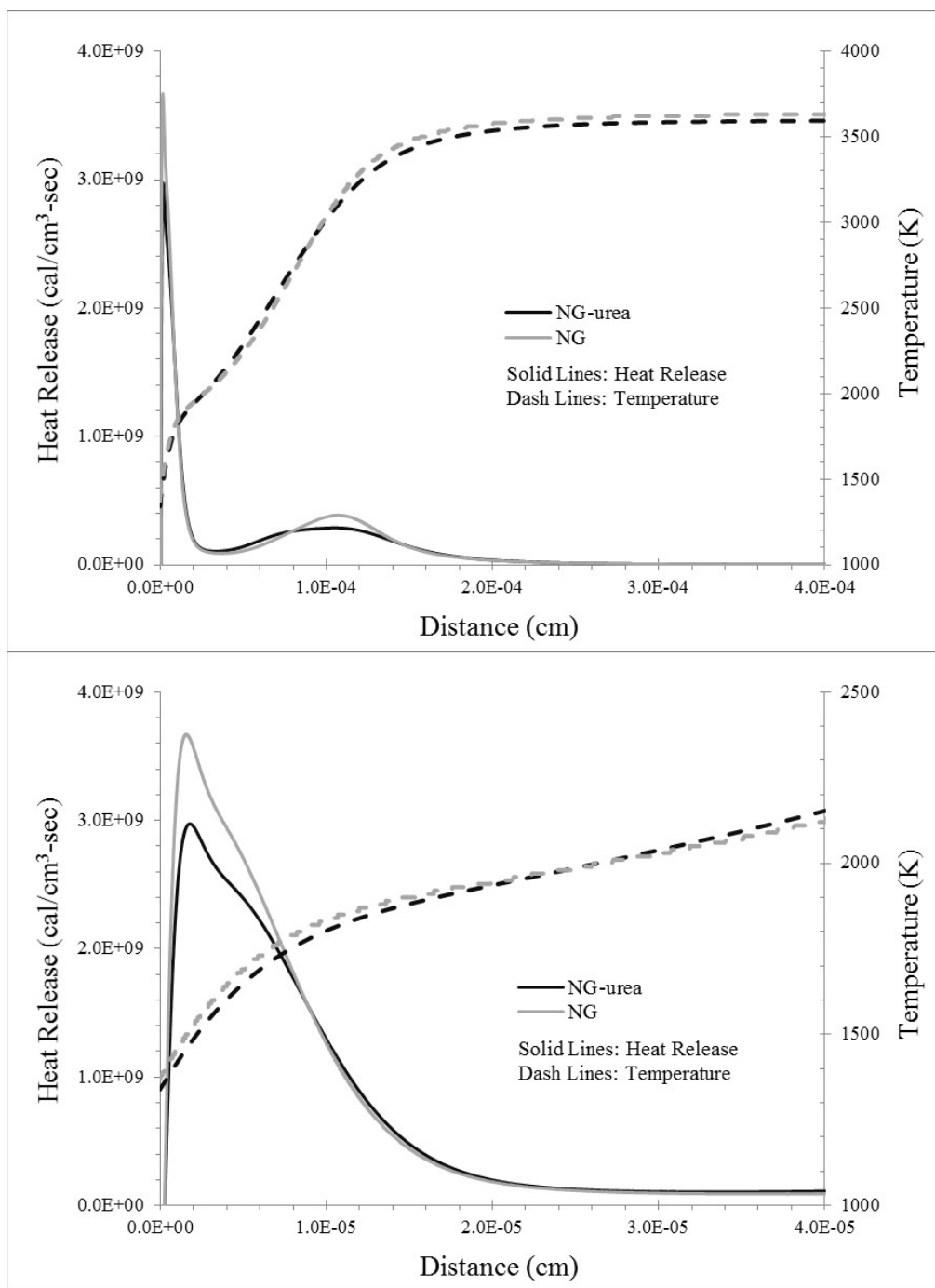


Fig. 19 PM/NPS-2 computed temperature and heat release vs. distance plots for NG-urea burning at 2000 atm

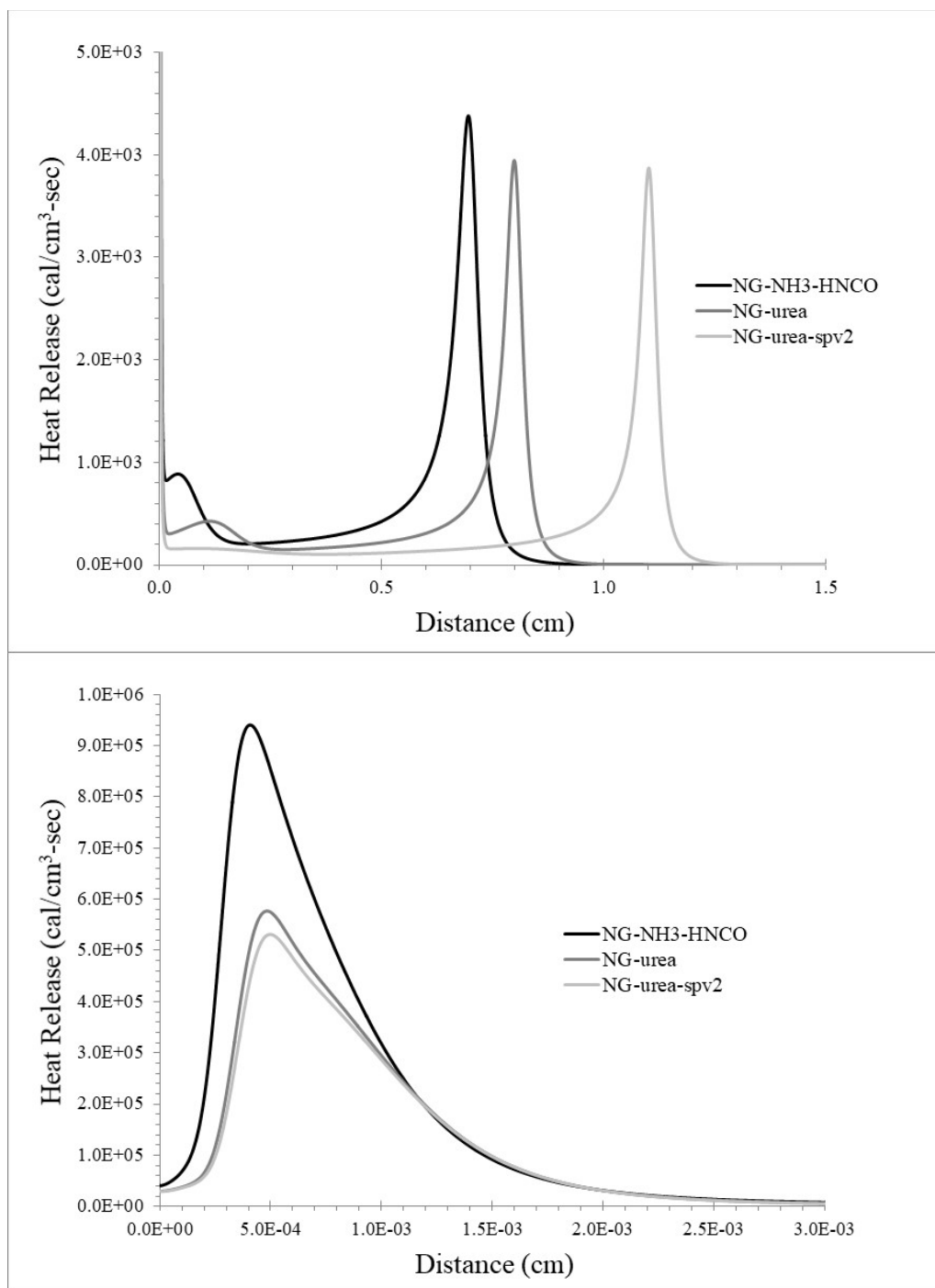


Fig. 20 PM/NPS-2 computed heat release vs. distance plots for NG-urea, NG-urea-spv2, and NG-NH₃-HNCO burning at 10 atm

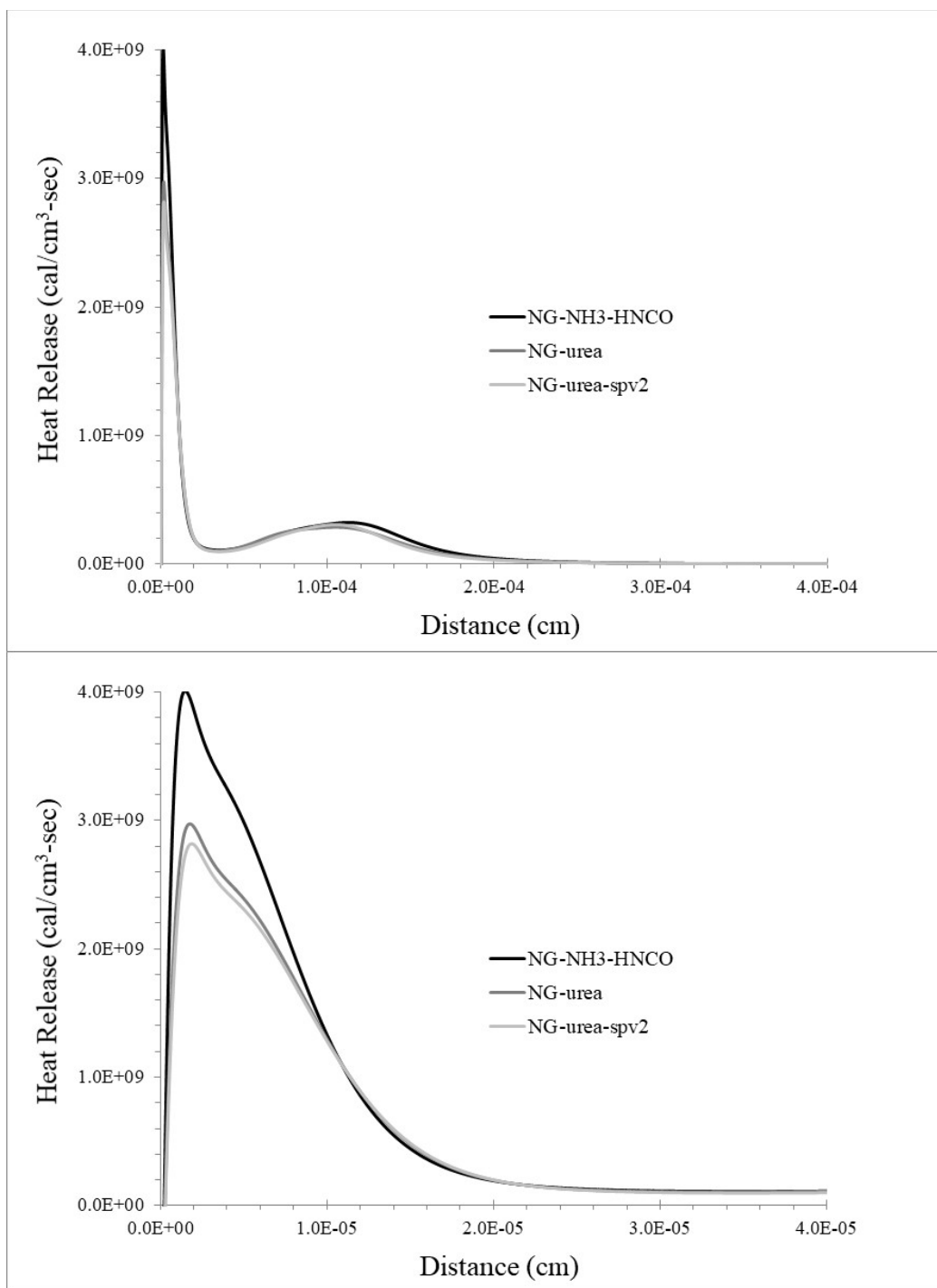
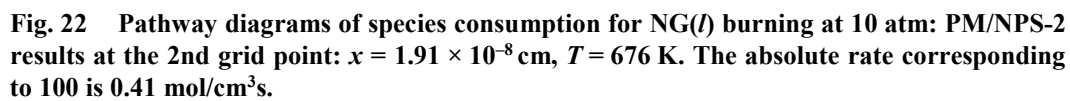


Fig. 21 PM/NPS-2 computed heat release vs. distance plots for NG-urea, NG-urea-spv2, and NG-NH₃-HNCO burning at 2000 atm

3.3 Pathway Diagrams and Sensitivity Analyses

This section presents pathway diagrams and S_i tabulations that identify chemical reactions that are important near the burning surface in the baseline simulations. The pathway diagrams were obtained from solutions produced by PM/NPS-2. Arrows indicate reactant–product connections. The widths of the arrows are proportional to the molar consumption rate ($-\dot{\omega}_k$) of the reactant (species) in the box at the arrow's tail. Species listed next to the arrows are co-reactants, and the numbers associated with them indicate the consumption rate of the reactant in the box due to its reaction with the co-reactant relative to the rate of all other reactions at that spatial location. Absolute rates are scaled to a range in which the value for the largest molar consumption rate produced by any reaction at the location is 100. To reduce clutter, reactions that produced molar consumption rates less than 5% of the maximum individual rate at the given location are not shown. (Moreover, they do not contribute to an arrow's width.) Hereafter, this threshold for inclusion in a diagram is referred to as the 5% cutoff level. Also note that, because the rates of consumption indicated by arrow widths in these diagrams correspond to the path's rate relative to the largest consumption rate due to one reaction *at that location*, direct comparison of arrow widths in different diagrams is not sufficient to infer differences in rates at different locations. The absolute rate corresponding to 100 in each diagram needs to be considered. For reference, those rates are provided in the figures' captions.

Figures 22–24 present pathway diagrams for the chemical (Eq. 6-based) consumption and/or production of prominent species near the surface obtained from PM/NPS-2's solution for NG(*l*) burning at 10 atm. As shown in Fig. 22, at the 2nd grid point, the species consumed at the highest rate was NO₂. It was produced by the unimolecular decompositions of NG(*g*), DICACOI [O₂NOCH₂CH(O•)CH₂ONO₂] and CACACOI [O₂NOCH₂CH(ONO₂)CH₂O•] and via some other minor channels. However, as can be inferred from the figure, the rate at which NO₂ was produced by reactions was significantly less than its rate of consumption by reactions. Indeed, further postprocessing of the solution revealed that diffusion was the primary source of NO₂ at this location. Approximately 6.15 mol/cm³s of the NO₂ that “appeared” at the 2nd grid point was attributable to that mechanism. Its appearance due to NO₂-producing reactions summed to approximately 0.22 mol/cm³s, and its disappearance due to NO₂-consuming reactions was greater. (That said, the primary mechanism for NO₂ loss from the location was convection.)



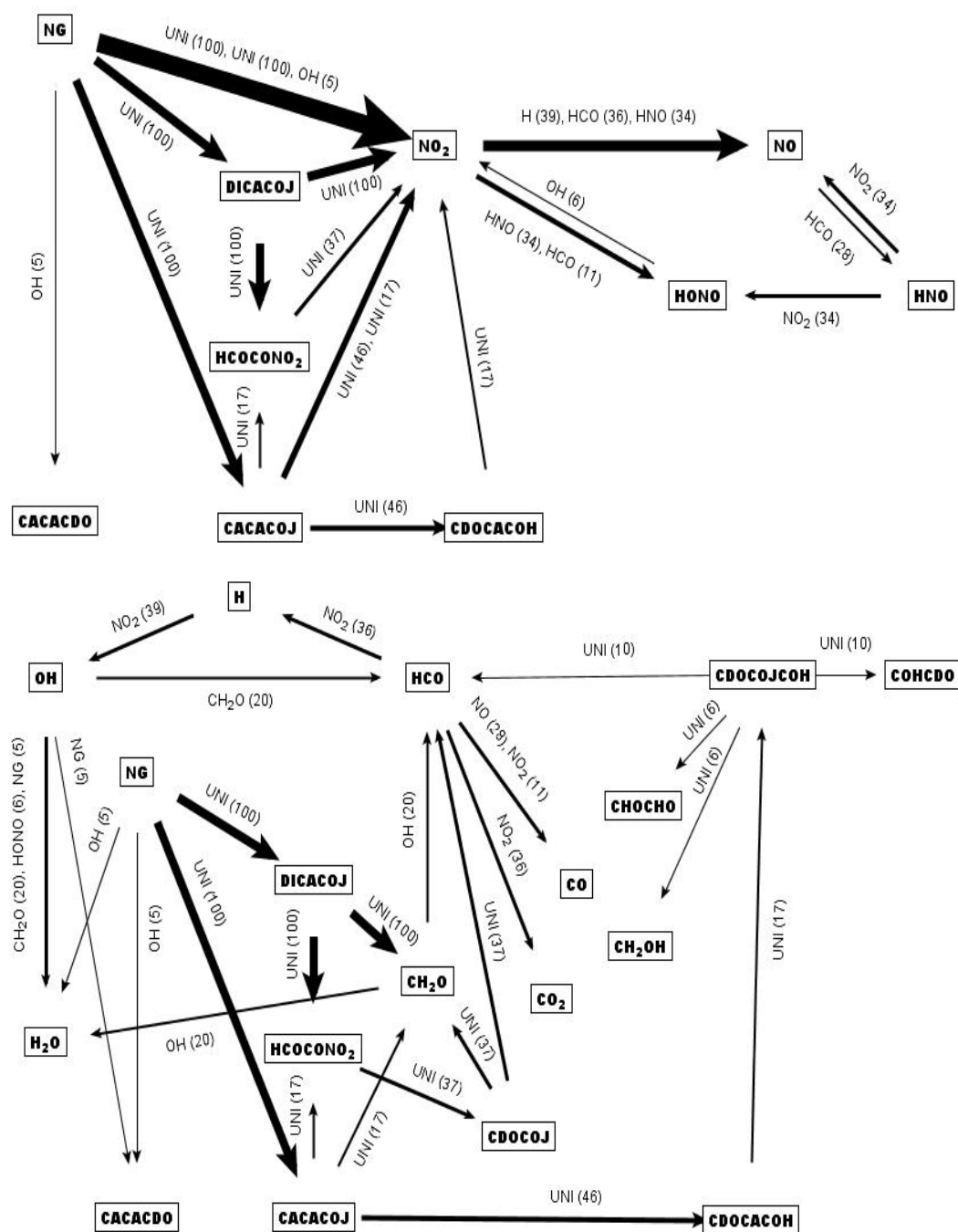


Fig. 23 Pathway diagrams of species consumption for NG(I) burning at 10 atm: PM/NPS-2 results at $x = 2.06 \times 10^{-6}$ cm, $T = 983$ K. The absolute rate corresponding to 100 is $8.1 \text{ mol/cm}^3\text{s}$.

The importance of diffusion as a source of NO_2 at the 2nd grid point would not have been notable had it been produced by a model that employed NPS-1. Corresponding to a scenario in which almost 9 out of 10 nitrate functional groups in $\text{NG}(I)$ scission at the surface and produce NO_2 , the dominance of a (physical) transport mechanism over chemical reactions would have been expected. However, the observation of diffusion's importance in the results produced by PM/NPS-2 gave us pause. At the temperatures in flames associated with the combustion of nitrate esters, species' production and consumption rates due to chemical reactions tend to be much higher than those due to diffusion. Suspecting that the NO_2 concentration gradient needed to drive diffusion was created by an acceleration in the rate at which NO_2 was produced via reactions downstream of the 2nd grid point, we plotted PM/NPS-2's and DZ/NPS-1's solutions for NO_2 mole fraction versus distance. Shown in Fig. 25, the results were consistent with our hypothesis. Near the surface, the orientation of the gradient predicted by PM/NPS-2 was opposite to the one predicted by DZ/NPS-1, and it drove NO_2 back toward the 2nd grid point.

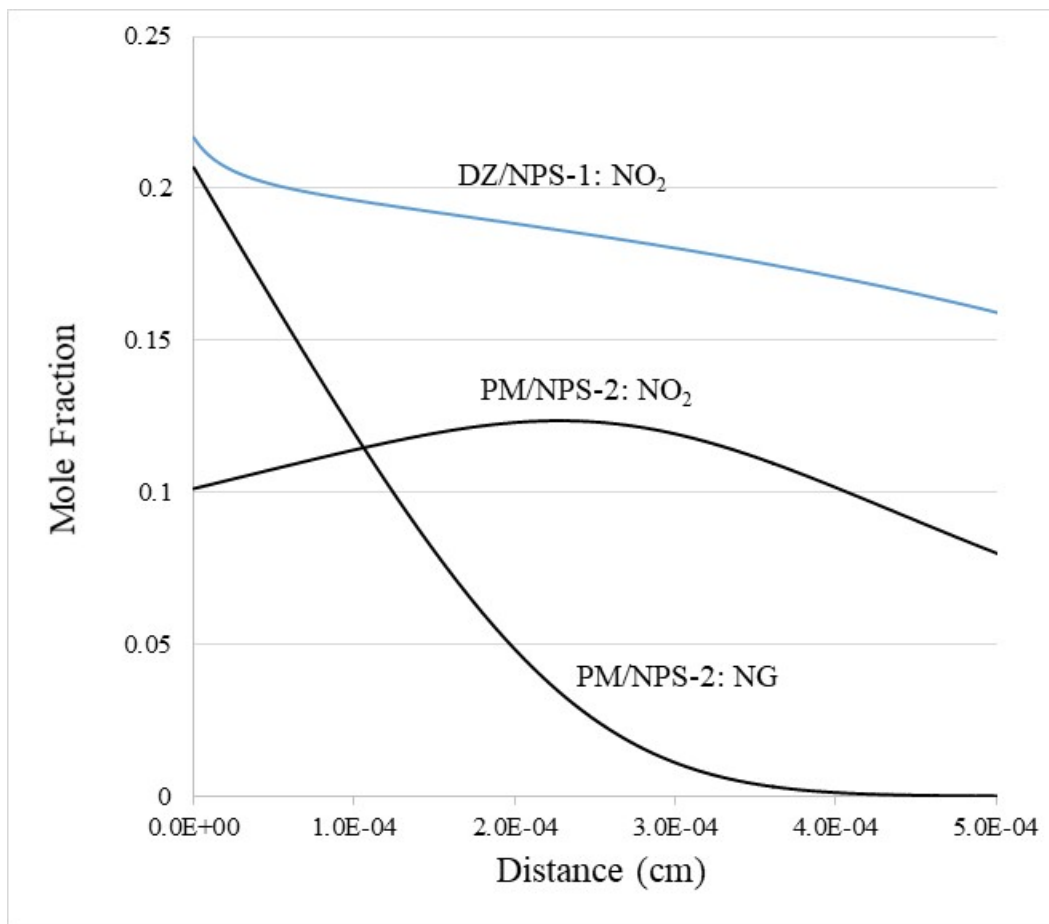
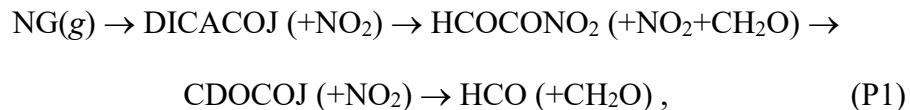


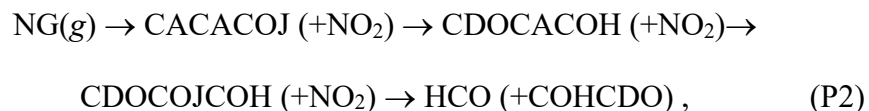
Fig. 25 NO_2 concentrations near the surface of $\text{NG}(I)$ burning at 10 atm: PM/NPS-2 results vs. DZ/NPS-1 results

Figure 23 provides additional insight into this finding. It shows that at a distance slightly downstream of the 2nd grid point (approximately 2.1 μm from the surface), but before the first $\dot{q}$ maximum was reached (approximately 4 μm from the surface), the chemical sources of NO_2 were still primarily unimolecular decompositions of NG(g) , DICACOI [$\text{O}_2\text{NOCH}_2\text{CH}(\text{O}\bullet)\text{CH}_2\text{ONO}_2$] and CACACOI [$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}\bullet$]. However, the temperature at this location was over 300 K higher than it was at the 2nd grid point, promoting a large increase in the absolute molar consumption rates of these species, and a concomitant increase in the production of NO_2 . (Based on the absolute consumption rate corresponding to a relative rate of 100 in Fig. 22 [$0.41 \text{ mol/cm}^3\text{s}$] and Fig. 23 [$8.1 \text{ mol/cm}^3\text{s}$] and the relative consumption rates of NG(g) , DICACOI , and CACACOI via unimolecular reactions that are listed, the rate of production of NO_2 via these reactions was about 300 times faster approximately 2.1 μm from the surface than it was directly adjacent to the surface.) Moreover, this increase was not completely offset by an increase in the rate of NO_2 's consumption via reactions with other species. Thus, the conditions were such that a (positive) gradient formed.

Another species of note in Figs. 22–24 is the important radical HCO . Reactions involving it are fast and highly exothermic, and like NO_2 , HCO 's concentration at the surface in the solutions produced by DZ/NPS-1 (and similar previous models) was suspected to be unrealistically high because its concentration in NPS-1 was unrealistically high. (Again, we note the basis for specifying NPS-1 was not “realism” per se. The foremost consideration was the attainment of reasonable agreement between measured and calculated burning rates.) As Figs. 22–24 show, HCO was produced from NG(g) via DICACOI [$\text{O}_2\text{NOCH}_2\text{CH}(\text{O}\bullet)\text{CH}_2\text{ONO}_2$] and CACACOI [$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}\bullet$] in as few as three steps. More importantly, however, from the 2nd grid point out to the first $\dot{q}$ maximum (at approximately 4 μm), the rates of paths to HCO 's formation via unimolecular decomposition steps,



and



increased significantly. Both paths produced a net (+1) increase in highly reactive radicals as well as three (less reactive) NO_2 molecules, and thus were strong

determinants of the burning rate. However, the rates through P1 were faster, and thus better promoted the global reaction rate than P2.

Table B-1 in Appendix B lists, for NG(*l*) burning at 10 atm, reactions whose $|S_i|$ at the 2nd grid point were at least 5% of the maximum single value. The differences between DZ/NPS-1's and PM/NPS-1's listings were generally small, as was expected. The similarities between those listings and PM/NPS-2's listing were somewhat surprising to us. (Given Miller and Anderson's [2004] success in reproducing burning rates for nitrate-ester-based propellants based on mechanisms that only included reactions involving small molecules, perhaps the similarities should have been expected.) With respect to the $|S_i|$ of reactions that are in both DZ and PM, only S_{R200} , S_{R94} , and S_{R350} were considerably different, and the net effect of the differences was small. We presume that the increase in R200's negative impact on $\dot{q}$ was offset by the increase in R94's positive impact and the reduction in R350's negative impact.

Two reactions of note in the listing for PM/NPS-2 are RL776 and RL778. RL776 prescribed the first step of P1, which is the scission of the O–NO₂ bond of the nitrate group attached to the secondary C-atom of NG [producing DICACOI = O₂NOCH₂CH(O•)CH₂ONO₂]. RL778 prescribed the first step of P2, which is the scission of the O–NO₂ bond of the nitrate group attached to either primary C-atom of NG [producing CACACOI = O₂NOCH₂CH(ONO₂)CH₂O•]. We observed this pair in listings for other mixtures and pressures and that, generally, S_{RL776} and S_{RL778} were similar in magnitude, but S_{RL776} was positive and S_{RL778} was negative. This was at first surprising because, given the similarities of P1 and P2, both of which produce very reactive intermediates, we surmised that either pathway alone could sustain combustion. (That is, if either RL776 or RL778 was removed from the mechanism and the simulation rerun, a burning rate prediction would be obtained and the S_i for the reaction that was kept would be positive.) As such, it suggested to us that the values reflected a competition between them for NG(g), with RL776 offering (by producing DICACOI) a more effective route for the production NO₂ and HCO than RL778. In this particular simulation, however, driven by NO₂ diffusing into the location, RL778's reverse rate was faster than its forward rate (see Fig. 22). Promoting an increase in NG(g)'s concentration, this factor likely played a role in producing the negative S_{RL778} .

That result notwithstanding, we still considered it likely that competition between RL776 and RL778 for NG(g) further downstream was also a factor. There, RL776/P1 and RL778/P2 both proceeded in the forward direction (see Figs. 23 and 24). In addition, examining terms contributing to the energy equation at the 2nd grid point, we found that heat transferred to it via conduction (5.0×10^5 cal/cm³s) was more than 10 times greater than the total produced by chemical reactions taking

place there (4.5×10^4 cal/cm³s), indicating the overall reaction rate downstream played a major role in producing heat at the 2nd grid point. Therefore, we reran the simulation with RL776 and RL778 (independently) eliminated, and observed what we expected. That is, when the simulation was run with RL776 eliminated, a burning rate was predicted, it was lower than the baseline (0.57 vs. 0.69 cm/s), and S_{RL778} was positive. It also proved to be “significant,” having a magnitude that was 8% of the maximum single value. When the simulation was run with RL778 eliminated, the predicted burning rate was higher than the baseline (0.77 vs. 0.69 cm/s), S_{RL776} was positive, and its magnitude was 10% of the largest single value. Taken together, these findings clearly indicate competition between RL776 and RL778 for NG(g), albeit not at the 2nd grid point, was a factor in producing the negative S_{RL778} in the baseline simulation.

Figures 26 and 27 illustrate paths by which prominent species were created and/or consumed near the surface in PM/NPS-2’s solution for NG(l) burning at 2000 atm. (Figure 26 corresponds to the 2nd grid point; Fig. 27 corresponds to the location of the first $\dot{q}$ maximum.) Unlike PM/NPS-2’s solution for NG(l) burning at 10 atm, adjacent to the burning surface the rates of unimolecular elimination of NO₂ from NG(g)—specifically RL776 and RL778, with the forward direction being dominant in both cases—far exceeded those of paths for the conversion of NO₂ to NO and HONO.

Table B-2 in Appendix B compares S_i at the 2nd grid point of the three models' solutions for NG(*l*) burning at 2000 atm. As might be expected, compared to the solutions for NG(*l*) burning at 10 atm, the shorter distance to complete combustion led to more small-molecule reactions having a significant impact on $\dot{q}$ near the surface. As was the case at 10 atm, for reactions that were in both PM and DZ, the differences between the S_i produced by DZ/NPS-1 and PM/NPS-1 were generally small. However, there were some large differences between the S_i produced by those two models and those produced by PM/NSP-2; S_{R261} , S_{R349} , S_{R229} , S_{RL352} , S_{R94} , S_{R195} , and S_{R170} were significant in the former and negligible in the latter. However, those differences can be rationalized. R261, R349, and R229 involved CH₂O, and CH₂O was a constituent of NPS-1. As a result, DZ/NPS-1 and PM/NPS-1 produced CH₂O concentrations adjacent to the surface that were much higher than those produced by PM/NSP-2, increasing the importance of reactions that involved it. RL352 involved NO₂, and R94, R195, and R170 involved NO, which could form in one step from NO₂. Like CH₂O, NO₂ was a constituent of NPS-1. Therefore, DZ/NPS-1 and PM/NPS-1 produced NO₂ concentrations near the surface that were much higher than those produced by PM/NSP-2, increasing the importance of reactions involving NO₂ and (indirectly) those involving NO. We also note that, even though RL778 ran in the forward direction and one might expect that increasing its rate would promote the forward rate of P2 and thus an increase in T , S_{RL778} was negative. Again, we believe this occurred because an increase in RL778's rate would have decreased the rate of consumption of NG(*g*) via RL776/P1, and RL776/P1 better promoted the global reaction rate than RL778/P2.

Table 8 compares S_i at the 2nd grid point of PM/NPS-2's solutions for NG(*l*) burning at 10 and 2000 atm. The comparison indicates that the rate-controlling (sub)mechanisms at the two pressures were significantly different. There are 30 reactions in the table, but only 11 were important at both pressures, and the S_i for one of those (R21) changed signs.

The difference in S_{R19} at the two pressures is particularly noteworthy. $|S_{R19}|$ was not large enough for R19 (HNO+NO=N₂O+OH) to be included in the 10 atm simulation's list of important reactions, but it had the largest value of the 2000 atm simulation's entire set. A similar increase in R19's importance with increase in pressure was previously observed by Miller and Anderson (2004). Finding also that R19 was an important determinant of d_{DZ} at low pressures, they attributed the change in R19's importance to the secondary flame moving closer to the surface with increase in pressure.

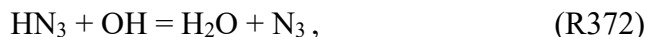
Table 8 Comparison of temperature sensitivity coefficients (S_i) for reactions that are important adjacent to the surface of NG(*l*) burning at 10 and 2000 atm: PM/NPS-2 results

Reaction	S_i			
	10 atm		2000 atm	
	Absolute	Relative	Absolute	Relative
(R3) $\text{H}+\text{NO}(+\text{M})=\text{HNO}(+\text{M})$	...	...	4.22E-08	5
(R4) $\text{NO}+\text{OH}(+\text{M})=\text{HONO}(+\text{M})$	3.46E-07	18	6.92E-08	9
(R19) $\text{HNO}+\text{NO}=\text{N}_2\text{O}+\text{OH}$	...	...	7.78E-07	100
(R21) $\text{HNO}+\text{NO}_2=\text{HONO}+\text{NO}$	3.03E-07	16	-1.46E-07	-19
(R23) $\text{HONO}+\text{OH}=\text{H}_2\text{O}+\text{NO}_2$	-4.92E-07	-26	-1.11E-07	-14
(R36) $\text{HCO}+\text{OH}=\text{H}_2\text{O}+\text{CO}$	-1.06E-07	-5	...	...
(R37) $\text{HCO}+\text{M}=\text{H}+\text{CO}+\text{M}$	2.18E-07	...	-1.10E-07	-14
(R43) $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$	...	11	3.29E-07	42
(R49) $\text{OH}+\text{H}_2=\text{H}_2\text{O}+\text{H}$	1.38E-07	7	5.43E-08	7
(R94) $\text{NO}_2+\text{H}=\text{NO}+\text{OH}$	4.60E-07	24	...	...
(R115) $\text{N}_2\text{O}+\text{O}=\text{NO}+\text{NO}$	...	...	4.18E-08	5
(R116) $\text{H}+\text{HNO}=\text{NH}+\text{OH}$	...	...	5.93E-08	8
(R160) $\text{HNO}+\text{OH}=\text{NO}+\text{H}_2\text{O}$	-1.48E-07	-8	-1.40E-07	-18
(R161) $\text{H}+\text{HNO}=\text{H}_2+\text{NO}$	-1.74E-07	-9	-1.30E-07	-17
(R165) $\text{NO}+\text{H}=\text{N}+\text{OH}$	...	...	8.17E-08	11
(R186) $\text{CO}+\text{NO}_2=\text{NO}+\text{CO}_2$	...	...	2.27E-07	29
(R200) $\text{HCO}+\text{NO}=\text{HNO}+\text{CO}$	-1.40E-06	-72	-1.26E-07	-16
(R227) $\text{H}+\text{CH}_2\text{O}(+\text{M})=\text{CH}_2\text{OH}(+\text{M})$	1.24E-07	6	...	...
(R261) $\text{OH}+\text{CH}_2\text{O}=\text{HCO}+\text{H}_2\text{O}$	7.32E-07	38	...	...
(R350) $\text{HCO}+\text{NO}_2=\text{CO}+\text{HONO}$	-2.25E-07	-12	...	...
(R351) $\text{HCO}+\text{NO}_2=\text{H}+\text{CO}_2+\text{NO}$	1.93E-06	100	2.75E-07	35
(R353) $\text{CHOCHO}+\text{OH}=\text{H}_2\text{O}+\text{CO}+\text{HCO}$	1.26E-07	7	...	...
(RL628) $\text{CH}_2\text{O}+\text{OH}=\text{HCOOH}+\text{H}$	...	...	5.08E-08	7
(RL776) $\text{NG}=\text{DICAC}+\text{NO}_2$	5.14E-07	27	1.03E-07	13
(RL778) $\text{NG}=\text{CACAC}+\text{NO}_2$	-2.54E-07	-13	-8.95E-08	-12
(RL779) $\text{CACAC}=\text{HCOCONO}_2+\text{CH}_2\text{O}+\text{NO}_2$	1.72E-07	9	...	...
(RL780) $\text{CACAC}=\text{CDOCAC}+\text{NO}_2$	...	...	7.18E-08	9
(RL858) $\text{CDOC}+\text{COH}=\text{COHCDO}+\text{HCO}$	2.84E-07	15	...	...
(RL859) $\text{CDOC}+\text{COH}=\text{CHOCHO}+\text{CH}_2\text{OH}$	-2.18E-07	-11	...	...
(RL904) $\text{HCOCONO}_2=\text{CDOC}+\text{NO}_2$	2.95E-07	15	...	...

R19 is fairly exothermic [$\Delta H_{R19}(298) = -18.9$ kcal/mol], and it produced OH radicals and scavenged NO. NO consumed HCO via $\text{HCO} + \text{NO} = \text{HNO} + \text{CO}$ (R200), and nitroxyl (HNO) was much less reactive than HCO. As indicated by S_{R200} 's negative values, R200 reduced $\dot{q}$ at both 10 and 2000 atm, but its impact was smaller at the higher pressure. At 10 atm, $|S_{R200}|$ was 72% of the single highest value, making it the second largest in the set. At 2000 atm, it was only 16% of the single highest value—7th largest in the set.

Pathway diagrams for the consumption and/or production of prominent species at the 2nd grid point of PM/NPS-2's solution for NG–HN₃ burning at 10 atm are shown in Fig. 28. Table B-3 in Appendix B lists S_i at the 2nd grid point. Sixteen of the 23 reactions listed in Table B-1 [for NG(*l*) burning at 10 atm] are found in Table B-3. Reactions whose presence in the table is attributable to the addition of HN₃ are shown in bold type. Reactions that became less important with the addition of HN₃ are listed at the bottom of the table.

Comparing Fig. 28 with Fig. 22, we observed that the paths by which NG(*g*) decomposed to NO₂ and NO in the NG(*l*) and NG–HN₃ simulations were similar. However, HN₃ decomposed to azide (N₃) near the surface via,



and N₃ reacted rapidly with NO to produce N₂ and nitrous oxide (N₂O),



As shown in Table B-3, S_{R377} was strongly positive. This was somewhat surprising because R377 reduced radical pool growth. (N₃ and NO are radicals; N₂ and N₂O are closed-shell species.) However, it was highly exothermic: $\Delta H_{R377}(298) = -100$ kcal/mol. In addition, it formed N₂O, and as discussed in the following paragraph, reactions involving N₂O promoted the system's overall rate of reaction. Given that NG–HN₃'s burning rate was much higher than NG(*l*)'s, these findings are consistent with the hypothesis that increasing the rate of NO's conversion to N₂ is a means for increasing burning rates. But, as will be discussed in Sections 3.4 and 3.5, a more important contributor to the increase appears to have been a general increase in reaction rates attributable to NG–HN₃'s high $h_c^{-\infty}$.

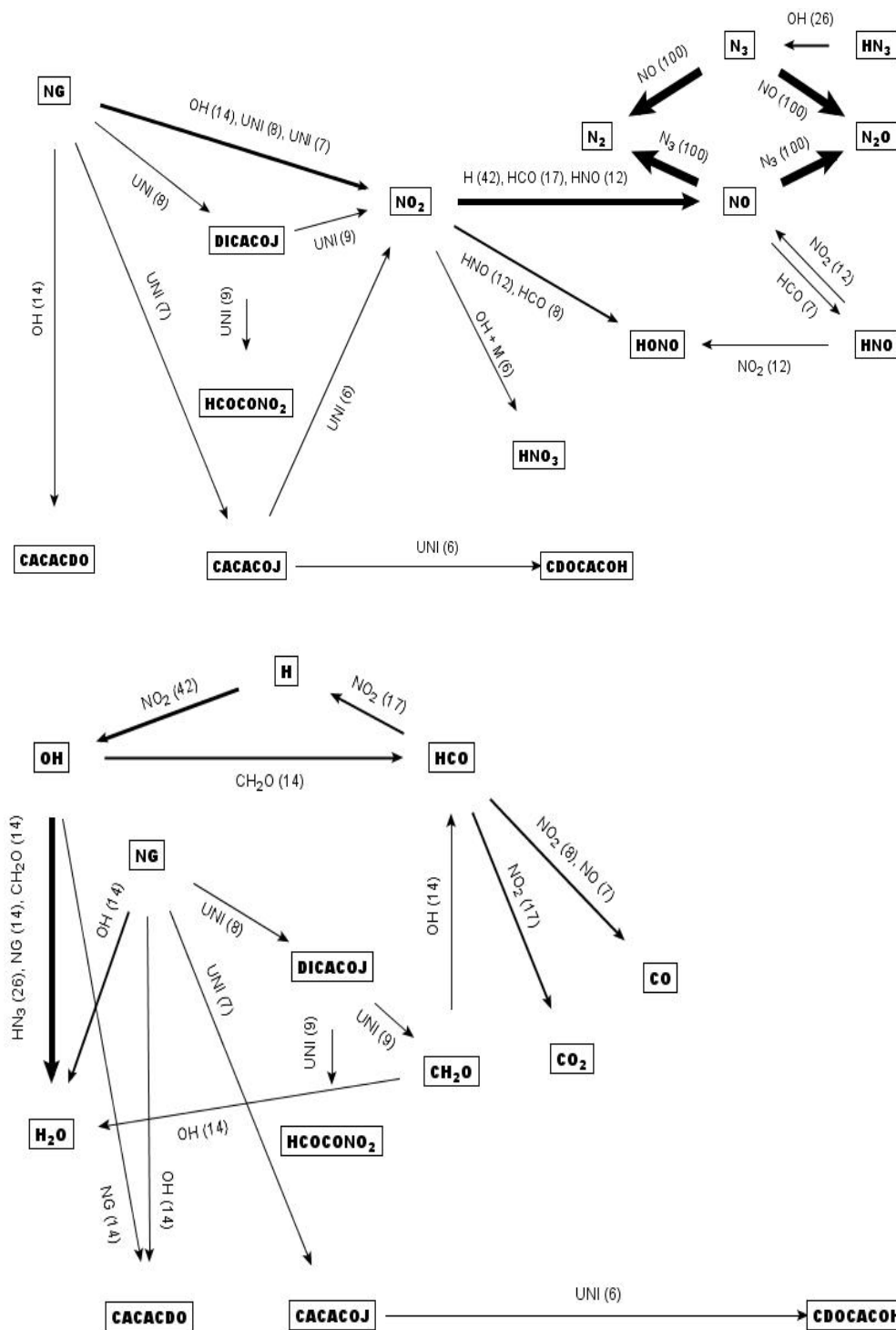
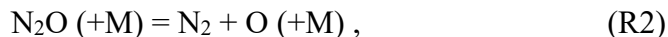


Fig. 28 Pathway diagrams of species consumption for NG-HN₃ burning at 10 atm; PM/NPS-2 results at the 2nd grid point: $x = 2.38 \times 10^{-8}$ cm, $T = 791$ K. The absolute rate corresponding to 100 is 9.6 mol/cm³s.

Reactions that are not observed in Fig. 28 because their rates did not reach the 5% cutoff level required for inclusion, but whose importance was indicated on the basis of large, positive S_i , included:



HN_3 's rate of decomposition via R369 was much slower than it was via R372. However, S_{R369} was more positive than S_{R372} (at the 2nd grid point). This was presumably due to R369 promoting radical pool growth by producing a radical (imidogen [NH]) from a closed-shell reactant (HN_3). R372 was radical production neutral. R2 also promoted radical pool growth. R111 was radical production neutral, but it was highly exothermic [$\Delta H_{\text{R111}}(298) = -62.3$ kcal/mol].

Pathway diagrams for the consumption and/or production of prominent species at the 2nd grid point of PM/NPS-2's solution for NG- HN_3 burning at 2000 atm are shown in Fig. 29. Per Table B-4, and as at 10 atm, R372, R377, R369, R2, and R111 were important determinants of the temperature gradient at the surface. But S_{R372} changed signs. Searching for an explanation for this surprising result, we observed in Fig. 29 that, compared to the solution at 10 atm, the rate at which HN_3 decomposed via R369 increased significantly relative to the rate it decomposed via R372. This suggested that the negative impact of increasing the rate of R372 occurred because it reduced the rate of HN_3 's decomposition via R369. As already noted, R369 promoted radical pool growth and R372 did not.

We also note that at 2000 atm, the $|S_i|$ for RL778, RL776, and RL780 in the solution for NG- HN_3 were much greater than they were in the comparable solution for NG(*l*). As observed in the solution for NG(*l*), the magnitudes of S_{RL776} and S_{RL778} were similar, with S_{RL776} being positive and S_{RL778} being negative. Having already surmised from the solution for NG(*l*) that the values were due to RL778 and RL776 offering competing paths for the production of NO_2 and HCO from NG(*g*), we surmised that the larger (relative) values of $|S_{\text{RL776}}|$ and $|S_{\text{RL778}}|$ in the solution for NG- HN_3 arose because the difference in the rates at which CACACIJ and DICACIJ could subsequently decompose to them was greater at the higher temperatures near the surface in the solution for NG- HN_3 . Inspection of Fig. 29 corroborated this hypothesis.

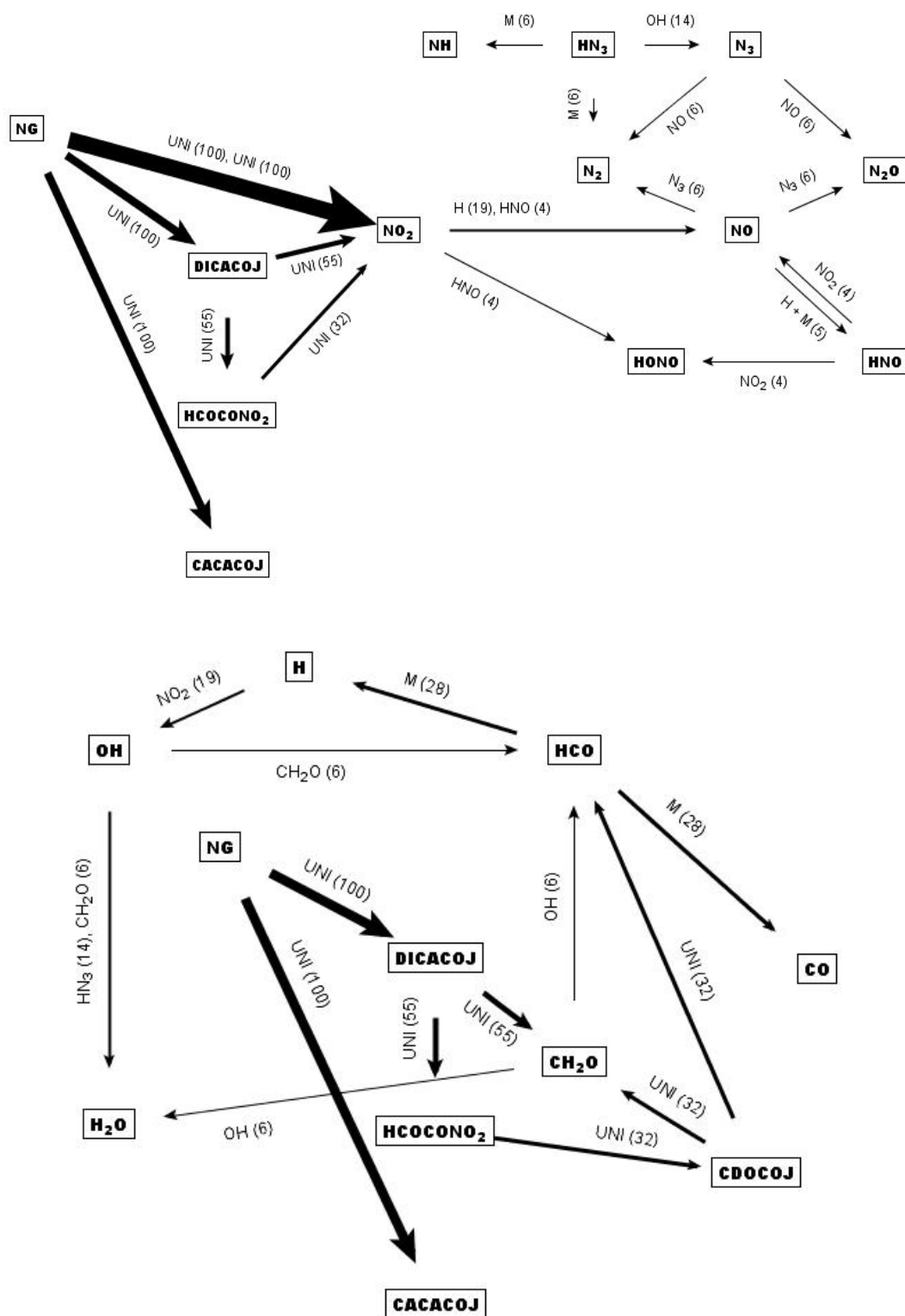
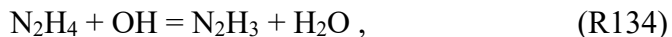


Fig. 29 Pathway diagrams of species consumption for NG-HN₃ burning at 2000 atm; PM/NPS-2 results at the 2nd grid point: $x = 3.26 \times 10^{-10}$ cm, $T = 2122$ K. The absolute rate corresponding to 100 is 1.0 mol/cm³s.

Pathway diagrams for the consumption and/or production of species at the 2nd grid point of PM/NPS-2's solutions for NG–N₂H₄ burning at 10 and 2000 atm are shown in Figs. 30 and 31, respectively. As was observed for NG–HN₃, the paths by which NG(g) decomposed in these simulations were similar to those found in the corresponding NG(*l*) simulation. At both pressures, the primary path for the decomposition of N₂H₄ was

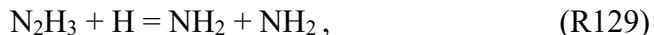


and the rate at which NO was converted to N₂ was again increased by products of the decomposition of the additive (N₂H₄). However, the increase was not as great as it was in the NG–HN₃ simulations.

Reactions that had relatively large $|S_i|$ at the 2nd grid point of PM/NPS-2's solutions for NG–N₂H₄ burning at 10 and 2000 atm are shown in Tables B-5 and B-6, respectively. As expected, R134 was in both lists, but S_{R134} was positive in the 10 atm simulation and negative in the 2000 atm simulation. The latter result was initially surprising, but could be rationalized. Besides R134, N₂H₄ decomposed via



and even though the rate of N₂H₄'s decomposition via R130 was less than its rate of decomposition via R134, S_{R130} was much greater than S_{R134} . Investigating this result, we noted that N₂H₃ produced by R134 primarily reacted with H-atoms via



producing two NH₂ molecules. Thus, the production of two NH₂ molecules via R134 and R129 involved the consumption of two radicals and, therefore, overall was radical production neutral. R130 also produced two NH₂ molecules, but did so in one step and thus promoted the radical pool's growth. Therefore, we presume S_{R134} was negative at 2000 atm because the increase in $\dot{q}$ due to N₂H₄'s decomposition via R130 would have diminished if the rate of N₂H₄'s decomposition via R134 was higher.

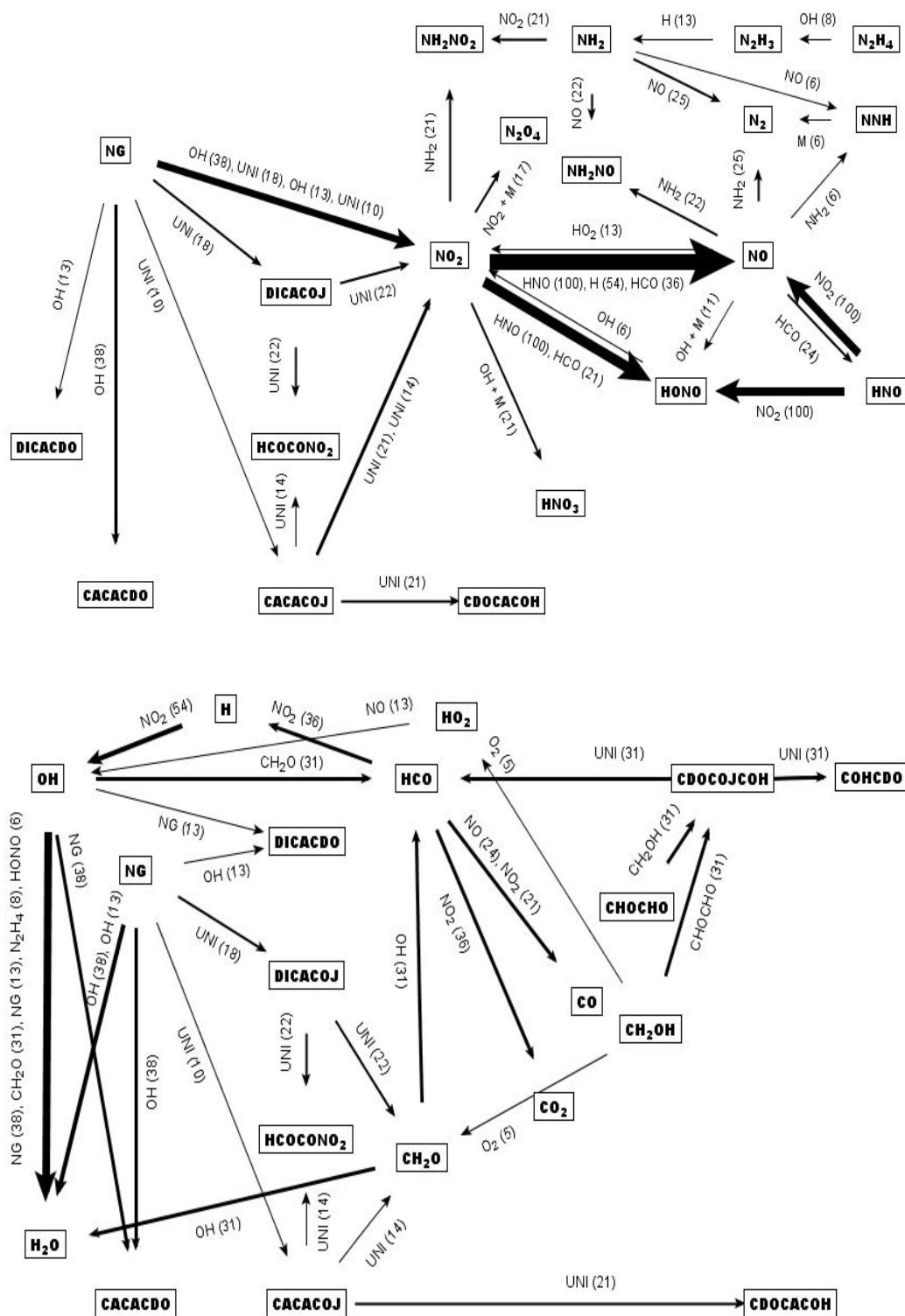
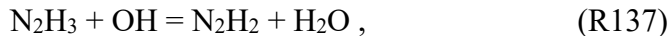
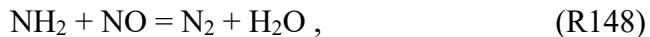
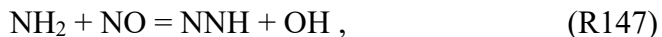


Fig. 30 Pathway diagrams of species consumption for NG-N₂H₄ burning at 10 atm; PM/NPS-2 results at the 2nd grid point: $x = 2.38 \times 10^{-8}$ cm, $T = 734$ K. The absolute rate corresponding to 100 is 0.47 mol/cm³s.

Other reactions whose $|S_i|$ increased (relative to others) with the addition of N_2H_4 included:



S_{R147} and S_{R148} were positive. Given that R148 reduced the radical pool's growth, its positive S_i was somewhat surprising. We presume it was a consequence of R148 being highly exothermic [$\Delta H_{R148}(298) = -124.7$ kcal/mol]. S_{R137} 's and S_{R162} 's negative values reflect the negative impact R137 and R162 had on the radical pool's growth.

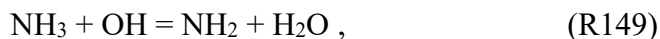
We also note that, as was the case for the solutions for NG– HN_3 , the $|S_i|$ for RL778 and RL776 were much greater in the solutions for NG– N_2H_4 than they were in the corresponding solution for NG(l). This (again) suggested that the difference in the rates at which CACAOJ and DICAOJ subsequently decomposed to HCO was greater at the higher temperatures near the surface in the solutions for NG– N_2H_4 . As shown in Fig. 30, the rates of HCO's production from these two species were indeed considerably different.

In addition to identifying mechanistic differences in the combustion of NG(l) and NG– N_2H_4 near their burning surfaces, we sought to explain the surprising result (mentioned in Section 3.2) that d_{DZ} in the solution for NG– N_2H_4 burning at 2000 atm was longer than d_{DZ} in the corresponding solution for NG(l). Although (as we have already noted) a change in d_{DZ} is not by itself a reliable indicator of kinetic activity, the temperature of the first stage was considerably higher in the solution for NG– N_2H_4 out to a distance well past the first $\dot{q}$ maximum in either simulation (see Fig. 9), and we thought that should have resulted in $d_{DZ}(NG-N_2H_4)$ being shorter than $d_{DZ}(NG(l))$.

Comparing species concentrations for the two cases in the range from 8.0×10^{-6} to 6.0×10^{-5} cm, where the former value corresponds to the end of the primary reaction zone and the latter corresponds to the onset of the second stage of the flame, we found that the concentration of NH_3 was significantly higher in the NG– N_2H_4 simulation. Produced by the radical-pool reducing reaction R162 (mentioned previously), which as at the 2nd grid point had a negative S_i in this region, it presumably reacted slowly and the net effect was a lengthening of the dark zone.

Pathway diagrams for the consumption and/or production of species at the 2nd grid point of PM/NPS-2's solution for NG–NH₃ burning at 10 atm are shown in Fig. C-1 in Appendix C. The primary paths for NG(*g*)'s decomposition in this system were similar to those for NG(*l*). No NH₃-producing or -consuming path is in the diagram because no reaction involving NH₃ had a rate that reached the 5% cutoff level needed for inclusion. (This was the reason for presenting the diagram in an appendix.)

Reactions with relatively large $|S_i|$ at the 2nd grid point of the solutions for NG–NH₃ burning at 10 and 2000 atm are shown in Tables B-7 and B-8, respectively. Reactions whose $|S_i|$ increased (relative to others) with the addition of NH₃ included:



R149 was the primary path for NH₃'s decomposition near the surface, but as can be inferred from its failure to be included in a pathway diagram, its rate was relatively low. (The rate of the unimolecular decomposition of NH₃ via NH₃(+M)=NH₂+H(+M) was even lower because the H₂N–H bond is very strong.) Moreover, as was noted in Section 3.2, R149 (with R147) was found to be an important (sub)mechanism for the release of heat immediately downstream of the first $\dot{q}$ maximum, suggesting that R149's (and therefore NH₃'s) ability to impact the burning rate was limited by its rate. As indicated in Table B-7, the mismatch between R149's rate and the rate of the primary mechanism driving deflagration was reduced when the system was modeled with PM/NPS-2, explaining why it predicted $r(\text{NG–NH}_3) > r(\text{NG}(\textit{l}))$ while DZ/NPS-1 and previous similar models did not.

As for R147 and R162, the signs of S_{R147} and S_{R162} were consistent with expectations based on radical pool growth or reduction; R147 increased the radical pool's concentration while R162 reduced it. However, the $|S_i|$ of these and other reactions whose magnitudes increased due to the addition of NH₃ were not very large.

Reactions with relatively large $|S_i|$ at the 2nd grid point of the solutions for NG–N₂ burning at 10 and 2000 atm are shown in Tables B-9 and B-10, respectively. Significant increases or decreases in $|S_i|$ attributable to the addition of N₂ were not observed. This result was not surprising. As already mentioned, N₂ is not chemically reactive at the temperatures expected in a flame produced by the

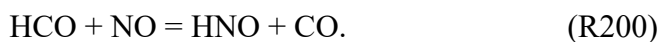
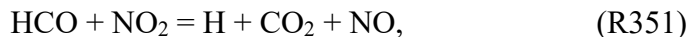
combustion of NG(*l*). However, it absorbed heat, reducing the temperature near the surface and thereby the burning rate.

Pathway diagrams for the consumption and/or production of species at the 2nd grid point of PM/NPS-2's solution for NG-HNCO burning at 10 atm are presented in Fig. C-2. The primary paths for NG(*g*)'s decomposition in this simulation were similar to those found in the corresponding NG(*l*) simulation. No HNCO-producing or -consuming path is in the diagram because no reaction involving HNCO had a rate that reached the 5% cutoff level needed for inclusion.

Reactions with relatively large $|S_i|$ at the 2nd grid point of the solutions for NG-HNCO burning at 10 and 2000 atm are shown in Tables B-11 and B-12, respectively. The S_i of all the reactions whose presence in these tables is attributable to the addition of HNCO are positive, but their magnitudes are at the low end of the range needed for inclusion. Moreover, S_{R200} and S_{R23} became more negative and S_{R94} and S_{R776} became less positive. This suggests that the kinetic activity induced by the addition of HNCO was limited, and as will be presented and discussed in Section 3.5, NG-HNCO's lower $h_c^{-\infty}$ appears to have been a more important factor in lowering the burning rate.

We also observed that $|S_{RL776}|$ and $|S_{RL778}|$ were not significant at 2000 atm. Given our observations concerning the relationship between RL776 and RL778, and that NG(*l*) and NG-HNCO burned at nearly the same rate at 2000 atm, this result was surprising. However, we did not seek an explanation.

Reactions with relatively large $|S_i|$ at the 2nd grid point of the solutions for NG-CH₂O burning at 10 and 2000 atm are shown in Tables B-13 and B-14, respectively. As was found for NG-N₂, the additive did not increase the $|S_i|$ of any reaction enough (relative to others) for them to be included therein. The orderings of reactions in these tables and those in the corresponding tables for NG(*l*) are somewhat different, but the specific effect the added CH₂O had on radical pool growth is not obvious. Because CH₂O reduced the burning rate, we searched for a radical pool-growth-reducing (sub)mechanism. A possibility was

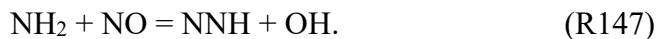
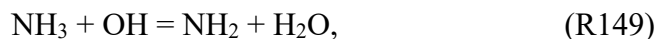


R261 was by far the most important reaction for the conversion of CH₂O to HCO. The rates of the three HCO-consuming reactions were comparable to each other.

R351 was radical production neutral. Producing only closed-shell species, R350 and R200 reduced the radical pool's growth. As such, CH₂O-induced promulgation of this (sub)mechanism had the potential to lower NG(*l*)'s burning rate. However, as will be discussed in Section 3.5, CH₂O's low $h_c^{-\infty}$ appears to have been the most important factor in lowering NG(*l*)'s burning rate.

Pathway diagrams for the consumption and/or production of species at the 2nd grid point of PM/NPS-2's solution for NG-urea burning at 10 atm are presented in Fig. C-3. No urea-producing or -consuming reaction had a rate that reached the 5% cutoff level needed for it to be included in a diagram.

Reactions with relatively large $|S_i|$ at the 2nd grid point of solutions for NG-urea burning at 10 and 2000 atm are shown in Tables B-15 and B-16, respectively. Reactions whose $|S_i|$ increased (relative to others) due to the addition of urea included:



NH₃ has been observed to be produced by the unimolecular decomposition of urea (Chen and Isa 1998), but the reaction in the mechanism that prescribed it did not appear in either table. We also note that H₂NC(O)NH produced via R384 could decompose to NH₂, but that path does not appear to have been important either. Indeed, the $|S_i|$ of all reactions whose inclusions in Tables B-15 and B-16 were attributable to the addition of urea were modest compared to those of reactions that were not. Therefore, even though all were positive, variations in the S_i of reactions important in the solutions for NG-urea and NG(*l*) as well as the difference in the two systems' $h_c^{-\infty}$ prevent a definitive assessment of the additive's overall impact on radical pool growth.

3.4 Variation of Selected Rate Coefficient Formulae A-Factors

To estimate kinetic activity's contribution to the observed burning rate changes, we reran DZ/NPS-1 simulations for some mixtures with the (Eq. 5) A_i for important additive decomposition reactions reduced or zeroed. Determinations of importance were made on the basis of the analyses presented in Section 3.3. The intent was to

make the additive chemically inert (like N₂) while retaining the influence of $h_c^{-\infty}$. The results are summarized in Table 9.*

The HN₃ decomposition reactions with the greatest influence on NG–HN₃'s burning rates were R369 (HN₃+M=NH+N₂+M) and R372 (HN₃+OH=H₂O+N₃). When NG–HN₃'s (baseline) 10 atm simulation was rerun with both A_{R369} and A_{R372} reduced by a factor of 10, the burning rate decreased 34%. When the 2000 atm simulation was rerun with A_{R369} reduced by a factor of 10, the rate decreased 7%. As such, these results suggested that kinetic activity did contribute to the burning rate increases effected by the addition of HN₃. However, given that NG–HN₃'s burning rates were more than 200% greater than NG(*l*)'s, those increases were due in large part to the increase in $h_c^{-\infty}$ that the addition of HN₃ produced.

At both 10 and 2000 atm, the N₂H₄ decomposition reaction with the greatest influence on NG–N₂H₄'s burning rate was R130 (N₂H₄=NH₂+NH₂). Reducing A_{R130} by a factor of 10 reduced NG–N₂H₄'s 10 atm burning rate 33%, which was about 50% of the total rate increase. In the 2000 atm simulation, this reduction reduced the burning rate 16%, which was about 20% of the total increase.

At both 10 and 2000 atm, the NH₃ decomposition reaction with the greatest influence on NG–NH₃'s burning rate was R149 (NH₃+OH=NH₂+H₂O). Reducing A_{R149} by a factor of 10 reduced NG–NH₃'s 2000 atm burning rate 14%. This difference was comparable to the difference in the burning rates predicted for NG–NH₃ and NG(*l*) at that pressure, suggesting kinetic activity was responsible for most of the observed increase.

* We note there is a fair degree of uncertainty in the reliability of the conclusions produced by this approach. As implemented, the reduction of the reactivity of additive molecule decomposition products by reducing A_i also reduced the reactivity of like products of the decomposition of NG(*l*). In addition, the reduction of the rate of one reaction could have been compensated for by an increase in the rate of another. Subsequent to an initial draft of this report, McQuaid and Chen (2016) devised and employed an approach that addresses these issues. We opted not to employ it for this study (and revise this section accordingly) because it would have required considerable effort, and that was not considered warranted because, corroborated by the results presented in Section 3.5, the results already obtained were considered sufficient for the study's scope and purpose.

Table 9 Predicted burning rates for NG(*l*) and NG–additive mixtures with the rates of key reactions reduced or zeroed: DZ-NPS-1 results

Mixture	Reaction	Change	<i>r</i> (cm/s)			
			10 atm		2000 atm	
			Baseline	w/ Change	Baseline	w/ Change
NG	...	...	1.08	...	30	...
NG–HN ₃	R369: HN ₃ +M = NH+N ₂ +M	$A_{R369} \rightarrow 0.1A_{R369}$	2.87	1.89 [–34%]	...	...
	R372: HN ₃ +OH = H ₂ O+N ₃	$A_{R372} \rightarrow 0.1A_{R372}$				
	R369: HN ₃ +M = NH+N ₂ +M	$A_{R369} \rightarrow 0.1A_{R369}$	...	...	135	126 [–7%]
NG–N ₂ H ₄	R130 NH ₂ +NH ₂ = N ₂ H ₄	$A_{R130} \rightarrow 0.1A_{R130}$	1.79	1.21 [–33%]	57	48 [–16%]
NG–NH ₃	R149: NH ₃ +OH = NH ₂ +H ₂ O	$A_{R149} \rightarrow 0.1A_{R149}$	...	...	36	31 [–14%]
NG–HNCO	R178: HNCO+OH = H ₂ O+NCO	$A_{R178} \rightarrow 0$	0.84	0.59 [–30%]	...	...
	R179: HNCO+OH = NH ₂ +CO ₂	$A_{R179} \rightarrow 0$				
	R101: NCO+NO = N ₂ O+CO	$A_{R101} \rightarrow 0$		0.64 [–24%]	...	...
	R178: HNCO+OH = H ₂ O+NCO	$A_{R178} \rightarrow 0.1A_{R178}$				
	R179: HNCO+OH = NH ₂ +CO ₂	$A_{R179} \rightarrow 0.1A_{R179}$		0.57 [–32%]	...	...
NG–urea	R384: H ₂ NC(O)NH ₂ +OH = H ₂ NC(O)NH + H ₂ O	$A_{R384} \rightarrow 0.1A_{R384}$	...	...	27	27 [0%]

The reactions with the greatest influence on NG–HNCO’s burning rates were R178 ($\text{HNCO} + \text{OH} = \text{H}_2\text{O} + \text{NCO}$), R179 ($\text{HNCO} + \text{OH} = \text{NH}_2 + \text{CO}_2$), and R101 ($\text{NCO} + \text{NO} = \text{N}_2\text{O} + \text{CO}$). When the 10 atm NG–HNCO simulation was rerun with both A_{R178} and A_{R179} zeroed, the burning rate was reduced 30%. And when A_{R101} was zeroed, the burning rate was reduced 24%. As such, these results indicate that even though NG–HNCO’s burning rate was 22% lower than NG(*l*)’s, the kinetic activity induced by HNCO was positive, offsetting the influence of the mixture’s $h_c^{-\infty}$. We do note, however, that PM/NPS-2-based results presented in Section 3.5 suggest HNCO’s potential to induce kinetic activity is less than that indicated by the results presented in Table 9.

For NG–urea burning at 2000 atm, R384 ($\text{H}_2\text{NC}(\text{O})\text{NH}_2 + \text{OH} = \text{H}_2\text{NC}(\text{O})\text{NH} + \text{H}_2\text{O}$) was the most important reaction for decomposing urea. Almost no change in the mixture’s burning rate resulted from reducing A_{R384} , suggesting the kinetic activity induced by urea was negligible at this pressure.

3.5 Changes to $h_c^{-\infty}$: PM/NPS-2 Results

To investigate the relationship between additive $h_c^{-\infty}$ s and their impact on NG(*l*)’s burning rate, we computed the burning rates of NG(*l*), NG–HN₃, NG–N₂H₄, NG–NH₃, NG–HNCO, NG–CH₂O, and NG–urea for a range of $h_c^{-\infty}$. Results are shown in Fig. 32. Differences produced for a given mixture follow expectations for the increase (decrease) in rate with increase (decrease) in mixture $h_c^{-\infty}$. However, the burning rates of different mixtures at a given value of $h_c^{-\infty}$ differed considerably. Indeed, Fig. 32 suggests a ranking of the kinetic activity (κ_a) induced by the additives: $\kappa_a(\text{N}_2\text{H}_4) > \kappa_a(\text{NH}_3) > \kappa_a(\text{urea}) \approx \kappa_a(\text{CH}_2\text{O}) > \kappa_a(\text{HNCO}) > \kappa_a(\text{HN}_3)$. A somewhat surprising result was that at each $h_c^{-\infty}$, the burning rates of all the mixtures except NG–HN₃ were greater than NG(*l*). While this could be taken to suggest that all the additives except HN₃ induced kinetic activity that promoted burning rate increases, it is also possible that the increased rates were due (in part) to the mixtures simply releasing more heat overall (at a given $h_c^{-\infty}$) because they were stoichiometric to CO₂, H₂O, and N₂ while NG(*l*) was slightly fuel lean.

Beyond demonstrating the importance of an additive’s $\Delta_f H_c$ in predicting the effect it will have on a formulation’s burning rate, these results also suggest another property of an additive that has the potential to impact an EM’s burning rate: namely, its affinity for the EM. Manifest as an enthalpy of mixing, it too will impact $h_c^{-\infty}$, and the impact could be significant. NG(*l*)’s heat capacity (and that of other nitrate esters [Miller 1997]) is approximately 0.3 cal/g-K (68 cal/mol-K). Therefore, a 1 kcal/mol change in $h_c^{-\infty}$ due to such interactions would be equivalent to a 15 K change in $T^{-\infty}$, and changes of such magnitude are known to have a

significant impact on burning rates. Since enthalpies of mixing with magnitudes 1 kcal/mol and larger are not uncommon, they are a property that should be considered when proposing/designing additives for an application.

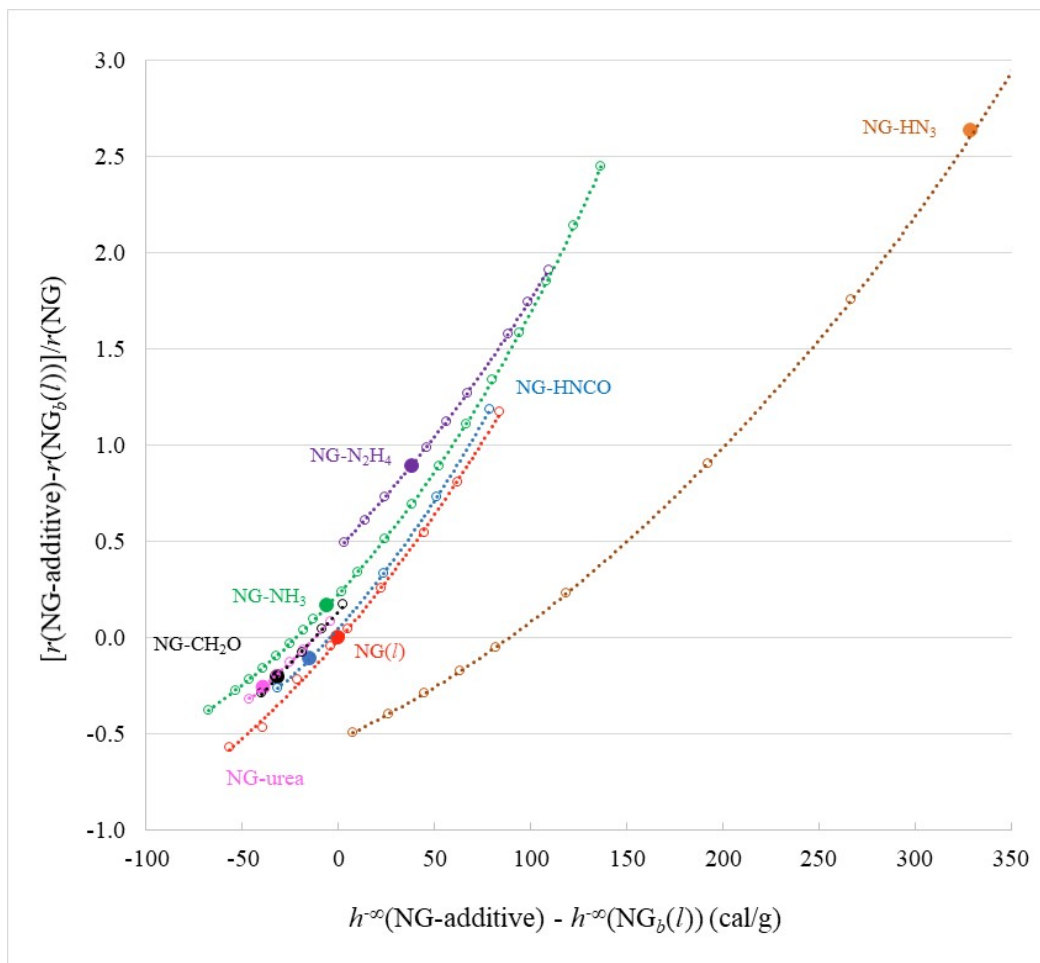


Fig. 32 Mixture burning rates at 10 atm as a function of h_c^∞ . $NG_b(l)$ is the baseline value for $NG(l)$. Filled-in markers are baseline values.

4. Summary and Conclusions

To elucidate the mechanisms by which various small-molecule additives impact the burning rates and flame structures of nitrate-ester-based EMs, the steady laminar deflagrations of $NG(l)$ and NG -additive mixtures were simulated with CYCLOPS-based models. The additives investigated were HN_3 , N_2H_4 , NH_3 , $HNCO$, N_2 , CH_2O , and urea. For this effort, we developed and employed a detailed finite-rate chemical kinetics mechanism (designated PM) that included parameters for computing the rates of elementary reactions for the decomposition of the parent molecule of every ingredient, including $NG(l)$. Enabling $NG(l)$'s conversion to a gas to be modeled as a nondissociative process [$NG(l) \rightarrow NG(g)$], it afforded for the

first time a capability for realistically simulating the gas-phase combustion chemistry occurring near the burning surface of a relatively large organic nitrate ester. Results produced by modeling NG(*l*)'s burning on this basis proved to offer new insights into the factors that control its burning rate and flame structure and these additives' impacts on them.

For continuity and comparison with previous CYCLOPS-based studies of nitrate ester deflagration, a detailed "small-molecule" chemical kinetics mechanism (designated DZ) that was similar to mechanisms employed in those studies was also developed and applied. Results were obtained with three mechanism/nascent product set models: DZ/NPS-1, PM/NPS-1, and PM/NPS-2, where NPS-1 corresponded to $\text{NG}(l) \rightarrow 2.6\text{NO}_2 + 0.4\text{HONO} + 2.0\text{CH}_2\text{O} + 0.6\text{HCO} + 0.4\text{CO}$, and NPS-2 corresponded to $\text{NG}(l) \rightarrow \text{NG}(g)$. Comparisons of $\dot{q}$ versus distance plots indicated NPS-1 reacted far more quickly and exothermically near the surface than NPS-2 (as one would expect). Nonetheless, for each mixture–pressure case that was simulated, DZ/NPS-1, PM/NPS-1, and PM/NPS-2 produced burning rate predictions that were in reasonable agreement with one another. Somewhat surprised by this finding, we analyzed differences between the simulations and found that, at the surface temperatures predicted, the energy needed to convert a unit mass of NG(*l*) into NG(*g*) was far less than that needed to convert the same mass to NPS-1. Therefore, NG(*g*)'s reactive potential did not have to be as great as NPS-1's to produce a similar burning rate prediction because less energy flux was required to produce the same mass flux. In addition, we found that the same small molecule reactions that had large temperature sensitivity coefficients near the surface in solutions produced by DZ/NPS-1 and PM/NPS-1 were large in the corresponding solution produced by PM/NPS-2. As such, these results explain (in part) the success Miller and Anderson (2004) had in reproducing the burning rates of nitrate-ester-based EMs using a model similar to DZ/NPS-1.

With respect to the additives' impacts on the burning rates and flame structures associated with NG(*l*)'s deflagration, we assumed when we started this study that they would act primarily by increasing the concentrations of some species, and thereby directly increase the rates of a subset of reactions within the network. Due to the sensitivity of reaction rates to changes in temperature, any change in $\dot{q}$ effected by that change would have the potential to be amplified by the remainder of the network. Calling it kinetic activity, we observed evidence for this mechanism in all the (baseline) mixtures, but found (generally) that it was more important at 10 atm than at 2000 atm, and the proportions of observed burning rate changes that were attributable to it were generally less than 50%. For NG–HN₃, which had the highest burning rates of all the mixtures for which they were computed, results obtained by reducing the A-factors of the rate coefficient formulae of important

reactions for the additives' decomposition suggested kinetic activity was responsible for $\leq 35\%$ of the total increase. Consistent with expectations, kinetic activity induced by N_2H_4 and NH_3 was significant.

Rather than kinetic activity, for all baseline mixtures except NG- NH_3 , the factor found to be most responsible for observed differences in predicted burning rates was the additive's $h_c^{-\infty}$. As observed previously by McQuaid and Chen (2014), this finding can be understood by recognizing that within the CYCLOPS framework (and other things being equal) increasing an EM's $h_c^{-\infty}$ by introducing an additive is equivalent to increasing its $h_c^{-\infty}$ by increasing its temperature. In the case of NG(*l*), a change in $h_c^{-\infty}$ of just 1 kcal/mol is equivalent to changing its temperature 15 K, and temperature changes of this magnitude are known to have a significant impact on burning rates. Therefore, the importance of $h_c^{-\infty}$ and the factors that underlie it should not be overlooked. In particular, aware that enthalpies of mixing with magnitudes 1 kcal/mol and larger are not uncommon, we postulate that they have the potential to have a strong influence on an EM-additive mixture's burning rate and, as such, should be considered when designing new propellant formulations.

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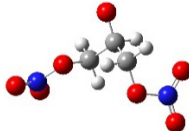
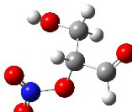
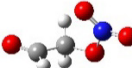
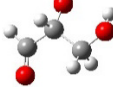
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Appendix A. Molecular Structure of Species in the PM Mechanism with Nonconventional Labels

In the interest of facilitating follow-on studies with the PM mechanism, some molecules in this report are referred to by the label employed for them in the CHEMKIN-format files that specify the mechanism. Unfortunately, the (standard) CHEMKIN framework limits the labels for species to ≤ 16 characters and does not permit the use of certain characters. Therefore, there are cases where it is not possible to assign a label that can be unambiguously translated into a molecular structure. Species referred to in the report whose molecular structures cannot be determined from the label referencing them are provided in Table A-1.

Table A-1 Molecular structures of species in the PM mechanism with nonconventional labels^a

Label	Stoichiometry	Multiplicity	Structure
DICACOJ	$C_3H_5N_2O_7$	2	
CACACOJ	$C_3H_5N_2O_7$	2	
CACACDO	$C_3H_4N_2O_7$	1	
CDOCACOH	$C_3H_5N_1O_5$	1	
HCOCONO2	$C_2H_3N_1O_4$	1	
CDOCOJCOH	$C_3H_5O_3$	2	
CDOCOJ	$C_2H_5O_2$	2	
COHCDO	$C_2H_4O_2$	1	

^a C-atoms are gray; H-atoms are white; N-atoms are blue; O-atoms are red.

Table A-1 Molecular structures of species in the PM mechanism with nonconventional labels^a (continued)

Label	Stoichiometry	Multiplicity	Structure
CHOCHO	C ₂ H ₂ O ₂	1	
CJOHCDO	C ₂ H ₃ O ₂	2	
HCOOH	C ₁ H ₂ O ₂	1	

^a C-atoms are gray; H-atoms are white; N-atoms are blue; O-atoms are red.

**Appendix B. Normalized Temperature Sensitivity Coefficients for
Reactions Important in Determining the Burning Rates of
NG(I) and NG–Additive Mixtures**

Appendix B presents tables of (logarithmic-derivative form) normalized temperature sensitivity coefficients (S_i) for reactions (i) at the 2nd grid point of steady laminar 1-D premixed flame solutions for CYCLOPS-based simulations of liquid nitroglycerine [NG(*l*)] and NG-additive deflagration. Results produced by DZ/NPS-1, PM/NPS-1, and PM/NPS-2 are presented. Only reactions with $|S_i|$ at least 5% of the single largest value at the location are listed. The reactions are ordered based on the results produced by the PM/NPS-2 model. In the tables for NG-additive mixtures, reactions that are in bold face are not in the list of reactions for the corresponding NG(*l*) solution.

Table B-1 Normalized temperature sensitivity coefficients at the 2nd grid point: NG(I) burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	4.25E-05	100	5.25E-06	100	1.93E-06	100
(R200) HCO+NO=HNO+CO	-1.59E-05	-37	-2.14E-06	-41	-1.40E-06	-72
(R261) OH+CH ₂ O=HCO+H ₂ O	1.65E-05	39	2.81E-06	54	7.32E-07	38
(RL776) NG=DICACOJ+NO ₂	...	...	...	...	5.14E-07	27
(R23) HONO+OH=H ₂ O+NO ₂	-1.17E-05	-28	-1.66E-06	-32	-4.92E-07	-26
(R94) NO ₂ +H=NO+OH	3.23E-06	8	3.96E-07	8	4.60E-07	24
(R4) NO+OH(+M)=HONO(+M)	1.64E-06	4	8.43E-07	16	3.46E-07	18
(R21) HNO+NO ₂ =HONO+NO	1.71E-06	4	3.93E-07	8	3.03E-07	16
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	2.95E-07	15
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	2.84E-07	15
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	-2.54E-07	-13
(R350) HCO+NO ₂ =CO+HONO	-2.15E-05	-51	-2.31E-06	-44	-2.25E-07	-12
(R43) CO+OH=CO ₂ +H	4.79E-07	1	1.43E-07	3	2.18E-07	11
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	-2.18E-07	-11
(R161) H+HNO=H ₂ +NO	-1.18E-06	-3	-2.24E-07	-4	-1.74E-07	-9
(RL779) CACACOJ=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	1.72E-07	9
(R160) HNO+OH=NO+H ₂ O	-8.84E-07	-2	-1.93E-07	-4	-1.48E-07	-8
(R49) OH+H ₂ =H ₂ O+H	2.62E-07	1	9.95E-08	2	1.38E-07	7
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	1.26E-07	7
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	-3.22E-07	-1	...	...	1.24E-07	6
(R36) HCO+OH=H ₂ O+CO	-1.91E-06	-5	-1.98E-07	-4	-1.06E-07	-6
(RL632) HCOOH=HCO+OH	...	...	-3.83E-07	-7	...	...
(RL352) OH+NO ₂ (+M)=HNO ₃ (+M)	...	...	-2.98E-07	-6	...	...

^a 2nd grid point $x = 9.42 \times 10^{-8}$ cm, $T = 719$ K.

^b 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 703$ K.

^c 2nd grid point $x = 1.91 \times 10^{-8}$ cm, $T = 676$ K.

Table B-2 Normalized temperature sensitivity coefficients at the 2nd grid point: NG(I) burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.12E-06	66	1.66E-07	82	7.78E-07	100
(R43) CO+OH=CO ₂ +H	7.81E-07	46	1.02E-07	50	3.29E-07	42
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.70E-06	100	2.03E-07	100	2.75E-07	35
(R186) CO+NO ₂ =NO+CO ₂	8.01E-07	47	1.01E-07	50	2.27E-07	29
(R21) HNO+NO ₂ =HONO+NO	-3.76E-07	-22	-5.13E-08	-25	-1.46E-07	-19
(R160) HNO+OH=NO+H ₂ O	-3.15E-07	-19	-4.61E-08	-23	-1.40E-07	-18
(R161) H+HNO=H ₂ +NO	-2.38E-07	-14	-3.37E-08	-17	-1.30E-07	-17
(R200) HCO+NO=HNO+CO	-9.12E-07	-54	-1.07E-07	-53	-1.26E-07	-16
(R23) HONO+OH=H ₂ O+NO ₂	-7.07E-07	-42	-9.78E-08	-48	-1.11E-07	-14
(R37) HCO+M=H+CO+M	-5.18E-07	-31	-6.52E-08	-32	-1.10E-07	-14
(RL776) NG=DICACOH+NO ₂	...	...	...	...	1.03E-07	13
(RL778) NG=CACACOH+NO ₂	...	...	...	...	-8.95E-08	-12
(R165) NO+H=N+OH	...	...	...	...	8.17E-08	11
(RL780) CACACOH=CDOCACOH+NO ₂	...	...	...	...	7.18E-08	9
(R4) NO+OH(+M)=HONO(+M)	4.84E-07	29	5.87E-08	29	6.92E-08	9
(R116) H+HNO=NH+OH	...	...	...	...	5.93E-08	8
(R49) OH+H ₂ =H ₂ O+H	1.67E-07	10	2.73E-08	14	5.43E-08	7
(RL628) CH ₂ O+OH=HCOOH+H	...	...	3.10E-08	15	5.08E-08	7
(R3) H+NO(+M)=HNO(+M)	-5.19E-08	-3	...	...	4.22E-08	5
(R115) N ₂ O+O=NO+NO	...	...	...	...	4.18E-08	5
(R261) OH+CH ₂ O=HCO+H ₂ O	4.87E-07	29	4.67E-08	23	...	...
(R349) CH ₂ O+NO ₂ =HCO+HONO	4.07E-07	24	4.80E-08	24	...	...
(R229) H+CH ₂ O=HCO+H ₂	-1.67E-07	-10	-2.80E-08	-14	...	...
(R94) NO ₂ +H=NO+OH	1.77E-07	10	1.88E-08	9	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	1.23E-07	7	1.79E-08	9	...	...
(R170) N ₂ O+NO=N ₂ +NO ₂	8.16E-08	5	1.06E-08	5	...	...
(RL352) OH+NO ₂ (+M)=HNO ₃ (+M)	...	...	1.22E-08	6	...	...

^a 2nd grid point $x = 1.53 \times 10^{-9}$ cm, $T = 1378$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1378$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1373$ K.

Table B-3 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–HN₃ burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	3.42E–05	100	1.76E–05	100	5.30E–06	100
(R377) N₃+NO=N₂+N₂O	9.27E–06	27	5.35E–06	31	2.87E–06	54
(R200) HCO+NO=HNO+CO	–1.38E–05	–40	–6.62E–06	–38	–2.49E–06	–47
(R261) OH+CH ₂ O=HCO+H ₂ O	1.51E–05	44	9.29E–06	53	1.71E–06	32
(R369) HN₃+M=NH+N₂+M	8.98E–06	26	5.95E–06	34	1.65E–06	31
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	1.61E–06	30
(R94) NO ₂ +H=NO+OH	3.75E–06	11	1.55E–06	9	1.59E–06	30
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	–1.51E–06	–29
(R2) N₂O(+M)=N₂+O(+M)	3.20E–06	9	2.35E–06	13	1.23E–06	23
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	1.10E–06	21
(R43) CO+OH=CO ₂ +H	1.72E–06	5	1.22E–06	7	9.93E–07	19
(R36) HCO+OH=H ₂ O+CO	–4.19E–06	–12	–1.92E–06	–11	–9.65E–07	–18
(R21) HNO+NO ₂ =HONO+NO	3.74E–06	11	2.11E–06	12	8.99E–07	17
(R372) HN₃+OH=H₂O+N₃	...	...	...	...	8.68E–07	16
(R111) N₂O+H=N₂+OH	...	...	1.02E–06	6	8.42E–07	16
(R352) CHOCHO(+M)=HCO+HCO(+M)	...	...	...	...	6.89E–07	13
(R49) OH+H ₂ =H ₂ O+H	...	...	1.10E–06	6	6.71E–07	13
(RL776) NG=DICACOJ+NO ₂	...	...	...	...	6.00E–07	11
(R229) H+CH ₂ O=HCO+H ₂	–2.75E–06	–8	–1.96E–06	–11	–6.00E–07	–11
(RL780) CACACOJ=CDOCACOH+NO₂	...	...	...	...	5.89E–07	11
(R161) H+HNO=H ₂ +NO	–2.38E–06	–7	–1.25E–06	–7	–5.83E–07	–11
(RL632) HCOOH=HCO+OH	...	...	–2.25E–06	–13	–5.35E–07	–10
(R354) CHOCHO+H=H₂+CO+HCO	...	...	...	...	–5.34E–07	–10
(R4) NO+OH(+M)=HONO(+M)	6.36E–06	19	3.81E–06	22	5.21E–07	10
(R350) HCO+NO ₂ =CO+HONO	–1.02E–05	–30	–4.66E–06	–27	–4.65E–07	–9
(R37) HCO+M=H+CO+M	1.98E–06	6	1.29E–06	7	3.99E–07	8
(R23) HONO+OH=H ₂ O+NO ₂	–9.28E–06	–27	–4.55E–06	–26	–3.98E–07	–8
(R113) NNH+O=NO+NH	1.29E–06	4	8.85E–07	5	3.70E–07	7
(R38) HCO+H=CO+H₂	–1.30E–06	–4	...	...	–3.38E–07	–6
(R349) CH ₂ O+NO ₂ =HCO+HONO	2.65E–06	8	1.72E–06	10	2.92E–07	6
(R358) HCO+HCO=CH ₂ O+CO	–2.79E–06	–8	–1.26E–06	–7	...	...
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	[–2.54E–07]	[–13]
(RL779) CACACOJ=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	[1.72E–07]	[9]
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	[1.26E–07]	[7]
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	[–3.22E–07]	[–1]	...	...	[1.24E–07]	[6]

^a 2nd grid point $x = 8.29 \times 10^{-8}$ cm, $T = 808$ K.

^b 2nd grid point $x = 4.77 \times 10^{-8}$ cm, $T = 801$ K.

^c 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 791$ K.

^d Values for NG(*I*) shown.

Table B-4 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–HN₃ burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R111) N2O+H=N2+OH	2.87E-06	86	3.69E-07	100	6.45E-07	100
(R43) CO+OH=CO2+H	3.33E-06	100	2.72E-07	74	5.87E-07	91
(R186) CO+NO2=NO+CO2	2.10E-06	63	2.16E-07	59	4.30E-07	67
(R377) N3+NO=N2+N2O	1.90E-06	57	2.22E-07	60	4.07E-07	63
(R369) HN3+M=NH+N2+M	1.92E-06	58	2.51E-07	68	3.75E-07	58
(RL778) NG=CACACIJ+NO2	...	...	...	...	-3.58E-07	-56
(RL776) NG=DICACIJ+NO2	...	...	...	...	3.48E-07	54
(RL780) CACACIJ=CDOCACOH+NO2	...	...	...	...	3.32E-07	52
(R628) CH2O+OH=HCOOH+H	...	...	2.31E-07	63	2.85E-07	44
(R132) NH+NO2=NO+HNO	-1.12E-06	-34	-1.44E-07	-39	-2.62E-07	-41
(R113) NNH+O=NO+NH	1.06E-06	32	1.46E-07	40	2.41E-07	38
(R109) NH+NO=N2+OH	9.96E-07	30	1.31E-07	36	2.26E-07	35
(R199) HNNO+M=N2+OH+M	1.01E-06	30	1.24E-07	34	2.17E-07	34
(R160) HNO+OH=NO+H2O	-9.18E-07	-28	-1.16E-07	-32	-2.22E-07	-34
(R19) HNO+NO=N2O+OH	7.14E-07	22	1.03E-07	28	2.08E-07	32
(R229) H+CH2O=HCO+H2	-6.32E-07	-19	-1.83E-07	-50	-2.04E-07	-32
(R161) H+HNO=H2+NO	-7.43E-07	-22	-1.05E-07	-29	-1.89E-07	-29
(R372) HN3+OH=H2O+N3	-9.49E-07	-29	-1.45E-07	-39	-1.86E-07	-29
(R49) OH+H2=H2O+H	5.47E-07	17	1.06E-07	29	1.80E-07	28
(R351) HCO+NO2=H+CO2+NO	1.19E-06	36	1.16E-07	31	1.80E-07	28
(R61) H+OH+M=H2O+M	-6.24E-07	-19	-7.82E-08	-21	-1.62E-07	-25
(R93) NO2+H=NO+OH	...	...	9.02E-08	25	1.33E-07	21
(R116) H+HNO=NH+OH	2.96E-07	9	5.26E-08	14	1.17E-07	18
(R37) HCO+M=H+CO+M	-5.94E-07	-18	-8.17E-08	-22	-1.18E-07	-18
(R2) N2O(+M)=N2+O(+M)	5.45E-07	16	6.21E-08	17	9.65E-08	15
(R170) N2O+NO=N2+NO2	4.81E-07	15	5.11E-08	14	7.87E-08	12
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	6.69E-08	10
(R352) CHOCHO(+M)=HCO+HCO(+M)	...	...	...	...	6.65E-08	10
(R165) NO+H=N+OH	...	...	2.66E-08	7	6.52E-08	10
(R4) NO+OH(+M)=HONO(+M)	3.19E-07	10	4.13E-08	11	6.13E-08	10
(RL859) CDOCOJCOH=CHOCHO+CH2OH	...	...	...	...	-6.56E-08	-10
(R51) O+H2=OH+H	1.78E-07	5	3.91E-08	11	5.79E-08	9
(R45) HO2+CO=CO2+OH	2.76E-07	8	2.61E-08	7	5.38E-08	8
(RL779) CACACIJ=HCOCONO2+CH2O+NO2	...	...	...	...	5.08E-08	8
(R374) N3+N3=N2+N2+N2	-2.02E-07	-6	-2.50E-08	-7	-5.02E-08	-8

^a 2nd grid point $x = 1.43 \times 10^{-9}$ cm, $T = 2137$ K.

^b 2nd grid point $x = 1.72 \times 10^{-10}$ cm, $T = 2176$ K.

^c 2nd grid point $x = 3.26 \times 10^{-10}$ cm, $T = 2122$ K.

Table B-4 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–HN₃ burning at 2000 atm (continued)

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R3) H+NO(+M)=HNO(+M)	–3.59E–07	–11	–2.77E–08	–8	–4.96E–08	–8
(R147) NH₂+NO=NNH+OH	1.80E–07	5	2.76E–08	8	4.80E–08	7
(R198) HNNO+M=H+N₂O+M	2.17E–07	7	2.69E–08	7	4.56E–08	7
(RL632) HCOOH=HCO+OH	...	...	2.60E–08	7	4.44E–08	7
(R349) CH ₂ O+NO ₂ =HCO+HONO	5.32E–07	16	4.38E–08	12	4.38E–08	7
(R195) HNO+NO+NO=HNNO+NO ₂	–1.96E–07	–6	–2.20E–08	–6	–4.34E–08	–7
(R36) HCO+OH=H₂O+CO	–1.98E–07	–6	–2.27E–08	–6	–4.40E–08	–7
(RL636) HCOOH+OH=H₂O+CO₂+H	...	...	2.90E–08	8	4.04E–08	6
(R261) OH+CH ₂ O=HCO+H ₂ O	1.48E–06	44	...	...	...	...
(R206) O+CH₂O=OH+HCO	1.88E–07	6	...	...	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(R21) HNO+NO ₂ =HONO+NO	[–3.76E–07]	[–22]	[–5.13E–08]	[–25]	[–1.46E–07]	[–19]
(R200) HCO+NO=HNO+CO	[–9.12E–07]	[–54]	[–1.07E–07]	[–53]	[–1.26E–07]	[–16]
(R23) HONO+OH=H ₂ O+NO ₂	[–7.07E–07]	[–42]	[–9.78E–08]	[–48]	[–1.11E–07]	[–14]
(RL628) CH ₂ O+OH=HCOOH+H	...	...	[3.10E–08]	[15]	[5.08E–08]	[7]
(R3) H+NO(+M)=HNO(+M)	[–5.19E–08]	[–3]	...	...	[4.22E–08]	[5]

^a 2nd grid point $x = 1.43 \times 10^{-9}$ cm, $T = 2137$ K.

^b 2nd grid point $x = 1.72 \times 10^{-10}$ cm, $T = 2176$ K.

^c 2nd grid point $x = 3.26 \times 10^{-10}$ cm, $T = 2122$ K.

^d Values for NG(*l*) shown.

Table B-5 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–N₂H₄ burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	4.45E–05	100	7.52E–06	100	3.93E–06	100
(R200) HCO+NO=HNO+CO	–2.29E–05	–52	–3.91E–06	–52	–2.74E–06	–70
(R261) OH+CH ₂ O=HCO+H ₂ O	1.99E–05	45	4.36E–06	58	1.55E–06	39
(R147) NH₂+NO=NNH+OH	7.13E–06	16	1.69E–06	23	1.33E–06	34
(R21) HNO+NO ₂ =HONO+NO	5.82E–06	13	1.25E–06	17	9.28E–07	24
(RL776) NG=DICACOJ+NO ₂	...	...	...	...	8.54E–07	22
(R94) NO ₂ +H=NO+OH	3.72E–06	8	5.18E–07	7	8.19E–07	21
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	7.63E–07	19
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	7.05E–07	18
(R129) NH₂+NH₂=N₂H₃+H	3.04E–06	7	7.33E–07	10	6.83E–07	17
(R130) NH₂+NH₂=N₂H₄	3.91E–06	9	1.00E–06	13	6.49E–07	17
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	–6.78E–07	–17
(R23) HONO+OH=H ₂ O+NO ₂	–1.47E–05	–33	–2.64E–06	–35	–6.55E–07	–17
(R36) HCO+OH=H ₂ O+CO	–4.26E–06	–10	–6.46E–07	–9	–5.17E–07	–13
(R49) OH+H ₂ =H ₂ O+H	1.48E–06	3	4.47E–07	6	4.78E–07	12
(R4) NO+OH(+M)=HONO(+M)	6.68E–06	15	1.67E–06	22	4.73E–07	12
(R37) HCO+M=H+CO+M	4.40E–06	10	9.95E–07	13	4.64E–07	12
(R43) CO+OH=CO ₂ +H	...	...	3.15E–07	4	4.47E–07	11
(R161) H+HNO=H ₂ +NO	–2.75E–06	–6	–5.45E–07	–7	–4.29E–07	–11
(R148) NH₂+NO=N₂+H₂O	...	...	...	...	3.97E–07	10
(R350) HCO+NO ₂ =CO+HONO	–1.54E–05	–35	–2.35E–06	–31	–3.62E–07	–9
(RL632) HCOOH=HCO+OH	...	...	–8.67E–07	–12	–3.42E–07	–9
(R162) HNO+NH₂=NH₃+NO	–2.10E–06	–5	–4.44E–07	–6	–3.36E–07	–9
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	...	...	...	...	2.94E–07	7
(R134) N₂H₄+OH=N₂H₃+H₂O	1.59E–06	4	...	...	2.84E–07	7
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	–2.89E–07	–7
(R229) H+CH ₂ O=HCO+H ₂	–2.00E–06	–5	–5.76E–07	–8	–2.80E–07	–7
(R160) HNO+OH=NO+H ₂ O	–1.66E–06	–4	–3.44E–07	–5	–2.52E–07	–6
(RL779) CACACOJ=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	2.12E–07	5
(RL980) COHCDO+NO₂=CJOHCDO+HONO	...	...	...	...	2.03E–07	5
(R358) HCO+HCO=CH ₂ O+CO	–2.22E–06	–5	...	...	...	...
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	[1.26E–07]	[7]

^a 2nd grid point $x = 8.42 \times 10^{-8}$ cm, $T = 770$ K

^b 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 756$ K.

^c 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 734$ K.

^d Values for NG(*l*) shown.

Table B-6 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–N₂H₄ burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.06E–06	64	1.65E–07	85	4.57E–07	100
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.65E–06	100	1.93E–07	100	3.10E–07	68
(R43) CO+OH=CO ₂ +H	1.04E–06	63	1.11E–07	58	2.98E–07	65
(R186) CO+NO ₂ =NO+CO ₂	1.05E–06	63	1.25E–07	65	2.85E–07	62
(R147) NH₂+NO=NNH+OH	1.16E–06	70	1.72E–07	89	2.85E–07	62
(RL776) NG=DICACOOJ+NO ₂	...	...	...	...	2.76E–07	60
(RL778) NG=CACACOOJ+NO ₂	...	...	...	...	–2.65E–07	–58
(R129) NH₂+NH₂=N₂H₃+H	9.60E–07	58	1.12E–07	58	2.17E–07	48
(R130) NH₂+NH₂=N₂H₄	9.34E–07	57	1.11E–07	58	1.87E–07	41
(RL780) CACACOOJ=CDOCACOOH+NO ₂	...	...	...	...	1.78E–07	39
(R161) H+HNO=H ₂ +NO	–4.03E–07	–24	–6.29E–08	–33	–1.55E–07	–34
(R160) HNO+OH=NO+H ₂ O	–4.22E–07	–26	–6.15E–08	–32	–1.45E–07	–32
(R37) HCO+M=H+CO+M	–6.35E–07	–39	–8.17E–08	–42	–1.38E–07	–30
(R23) HONO+OH=H ₂ O+NO ₂	–7.04E–07	–43	–9.20E–08	–48	–1.25E–07	–27
(R200) HCO+NO=HNO+CO	–6.65E–07	–40	–7.13E–08	–37	–1.19E–07	–26
(R4) NO+OH(+M)=HONO(+M)	7.06E–07	43	8.83E–08	46	1.13E–07	25
(R49) OH+H ₂ =H ₂ O+H	2.85E–07	17	5.03E–08	26	9.98E–08	22
(RL628) CH ₂ O+OH=HCOOH+H	...	...	6.92E–08	36	9.97E–08	22
(R148) NH₂+NO=N₂+H₂O	3.70E–07	22	5.73E–08	30	9.41E–08	21
(R134) N₂H₄+OH=N₂H₃+H₂O	–2.65E–07	–16	–4.90E–08	–25	–9.75E–08	–21
(R137) N₂H₃+OH=N₂H₂+H₂O	–3.68E–07	–22	–3.56E–08	–19	–7.65E–08	–17
(R229) H+CH ₂ O=HCO+H ₂	–2.75E–07	–17	–5.63E–08	–29	–6.71E–08	–15
(R162) HNO+NH₂=NH₃+NO	–3.39E–07	–21	–4.34E–08	–23	–6.65E–08	–15
(R261) OH+CH ₂ O=HCO+H ₂ O	7.56E–07	46	6.26E–08	33	5.98E–08	13
(R436) HNNOH=NH₂NO	1.97E–07	12	3.44E–08	18	5.76E–08	13
(R21) HNO+NO ₂ =HONO+NO	...	...	...	...	–5.11E–08	–11
(R3) H+NO(+M)=HNO(+M)	–4.18E–07	–25	–3.55E–08	–18	–4.94E–08	–11
(RL779) CACACOOJ=HCOCONO₂+CH₂O+NO₂	...	...	...	...	4.77E–08	10
(R349) CH ₂ O+NO ₂ =HCO+HONO	3.86E–07	23	4.58E–08	24	4.66E–08	10
(R116) H+HNO=NH+OH	1.02E–07	6	1.56E–08	8	4.64E–08	10
(R111) N₂O+H=N₂+OH	9.69E–08	6	1.76E–08	9	4.50E–08	10
(R136) N₂H₃+H=N₂H₂+H₂	–1.97E–07	–12	–2.17E–08	–11	–4.37E–08	–10
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	4.14E–08	9
(R149) NH₃+OH=NH₂+H₂O	1.37E–07	8	2.12E–08	11	3.69E–08	8
(R199) HNNO+M=N₂+OH+M	...	...	1.69E–08	9	3.62E–08	8
(R94) NO ₂ +H=NO+OH	2.85E–07	17	5.00E–08	26	3.51E–08	8

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1646$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1644$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1591$ K.

Table B-6 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–N₂H₄ burning at 2000 atm (continued)

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R170) N ₂ O+NO=N ₂ +NO ₂	...	...	1.18E-08	6	3.00E-08	7
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	-3.77E-08	-8
(R442) NH ₂ NO+OH=HNNO+H ₂ O	...	...	-1.67E-08	-9	-2.96E-08	-7
(R352) CHOCHO(+M)=HCO+HCO(+M)	...	...	...	...	2.57E-08	6
(R354) CHOCHO+H=H ₂ +CO+HCO	...	...	...	...	-2.63E-08	-6
(R440) NH ₂ NO+H=HNNO+H ₂	...	...	-1.53E-08	-8	-2.53E-08	-6
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	2.48E-08	5
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	2.39E-08	5
(R153) HONO+NH ₂ =NO ₂ +NH ₃	-9.66E-08	-6	...	...	...	...
(R152) NH ₃ (+M)=NH ₂ +H(+M)	-9.33E-08	-6	-1.11E-08	-6	...	...
(R181) HNCO+H=NH ₂ +CO	-8.59E-08	-5	...	...	...	...
(R196) HNNO+NO=NNH+NO ₂	...	...	1.14E-08	6	...	...
(RL636) HCOOH+OH=H ₂ O+CO ₂ +H	...	...	1.05E-08	6	...	...
(RL140) N ₂ H ₃ +NH ₂ =N ₂ H ₂ +NH ₃	...	...	-1.01E-08	-5	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(R165) NO+H=N+OH	...	...	...	...	[8.17E-08]	[11]
(R115) N ₂ O+O=NO+NO	...	...	...	...	[4.18E-08]	[5]

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1646$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1644$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1591$ K.

^d Values for NG(*I*) shown.

Table B-7 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–NH₃ burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	2.11E–05	100	5.10E–06	100	2.65E–06	100
(R200) HCO+NO=HNO+CO	–8.40E–06	–40	–2.39E–06	–47	–2.03E–06	–77
(R149) NH₃+OH=NH₂+H₂O	1.29E–06	6	9.34E–07	18	1.13E–06	43
(R23) HONO+OH=H ₂ O+NO ₂	–6.67E–06	–32	–2.30E–06	–45	–8.55E–07	–32
(R261) OH+CH ₂ O=HCO+H ₂ O	8.10E–06	38	2.75E–06	54	8.44E–07	32
(R94) NO ₂ +H=NO+OH	1.81E–06	9	5.78E–07	11	8.18E–07	31
(R21) HNO+NO ₂ =HONO+NO	1.35E–06	6	7.32E–07	14	7.20E–07	27
(R4) NO+OH(+M)=HONO(+M)	1.59E–06	8	1.50E–06	29	5.81E–07	22
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	5.38E–07	20
(RL776) NG=DICACOJ+NO ₂	...	...	...	...	5.04E–07	19
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	4.41E–07	17
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	–4.32E–07	–16
(R147) NH₂+NO=NNH+OH	5.06E–07	2	3.24E–07	6	3.72E–07	14
(R161) H+HNO=H ₂ +NO	–7.85E–07	–4	–3.38E–07	–7	–3.46E–07	–13
(R160) HNO+OH=NO+H ₂ O	–6.16E–07	–3	–3.14E–07	–6	–2.98E–07	–11
(R37) HCO+M=H+CO+M	5.09E–07	2	2.94E–07	6	2.83E–07	11
(R350) HCO+NO ₂ =CO+HONO	–1.04E–05	–49	–2.00E–06	–39	–2.80E–07	–11
(R36) HCO+OH=H ₂ O+CO	–1.05E–06	–5	–2.73E–07	–5	–2.30E–07	–9
(RL632) HCOOH=HCO+OH	...	...	–4.69E–07	–9	–2.15E–07	–8
(R43) CO+OH=CO ₂ +H	2.48E–07	1	1.58E–07	3	1.97E–07	7
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	...	...	...	...	1.82E–07	7
(R162) HNO+NH₂=NH₃+NO	–2.02E–07	–1	...	...	–1.38E–07	–5
(R49) OH+H ₂ =H ₂ O+H	...	...	...	...	1.34E–07	5
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	[–2.54E–07]	[–13]
(RL779) CACACOJ=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	[1.72E–07]	[9]
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	[1.26E–07]	[7]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 716$ K.

^b 2nd grid point $x = 2.71 \times 10^{-8}$ cm, $T = 703$ K.

^c 2nd grid point $x = 2.84 \times 10^{-8}$ cm, $T = 687$ K.

^d Values for NG(*l*) shown.

Table B-8 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–NH₃ burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	8.88E–07	86	1.31E–07	100	9.22E–07	100
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.03E–06	100	1.22E–07	94	3.43E–07	37
(R149) NH₃+OH=NH₂+H₂O	9.96E–07	97	1.21E–07	93	3.40E–07	37
(R43) CO+OH=CO ₂ +H	3.62E–07	35	4.44E–08	34	2.96E–07	32
(R186) CO+NO ₂ =NO+CO ₂	4.31E–07	42	5.44E–08	42	2.49E–07	27
(R23) HONO+OH=H ₂ O+NO ₂	–8.65E–07	–84	–1.10E–07	–84	–2.48E–07	–27
(R161) H+HNO=H ₂ +NO	–2.63E–07	–26	–3.72E–08	–28	–2.22E–07	–24
(R160) HNO+OH=NO+H ₂ O	–2.97E–07	–29	–4.16E–08	–32	–1.98E–07	–22
(R4) NO+OH(+M)=HONO(+M)	6.26E–07	61	7.08E–08	54	1.77E–07	19
(R147) NH₂+NO=NNH+OH	3.27E–07	32	4.95E–08	38	1.77E–07	19
(RL776) NG=DICACOI+NO ₂	...	...	...	...	1.52E–07	17
(R200) HCO+NO=HNO+CO	–5.17E–07	–50	–5.82E–08	–44	–1.47E–07	–16
(R21) HNO+NO ₂ =HONO+NO	–1.67E–07	–16	–2.28E–08	–17	–1.46E–07	–16
(R37) HCO+M=H+CO+M	–3.30E–07	–32	–4.20E–08	–32	–1.40E–07	–15
(RL778) NG=CACACOI+NO ₂	...	...	...	...	–1.34E–07	–15
(RL780) CACACOI=CDOCACOH+NO ₂	...	...	...	...	1.33E–07	15
(R349) CH ₂ O+NO ₂ =HCO+HONO	4.09E–07	40	4.86E–08	37	7.94E–08	9
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	7.22E–08	8
(RL628) CH ₂ O+OH=HCOOH+H	...	...	1.89E–08	14	6.24E–08	7
(R116) H+HNO=NH+OH	...	...	...	...	6.23E–08	7
(RL859) CDOCOJCOH=CHOCHO+CH₂OH	...	...	...	...	–5.52E–08	–6
(R49) OH+H ₂ =H ₂ O+H	8.82E–08	9	1.28E–08	10	5.32E–08	6
(R94) NO ₂ +H=NO+OH	2.18E–07	21	2.50E–08	19	5.32E–08	6
(R171) N₂O+NO=N₂+NO₂	6.31E–08	6	8.51E–09	7	4.96E–08	5
(R229) H+CH ₂ O=HCO+H ₂	–1.20E–07	–12	–1.90E–08	–15	...	...
(R162) HNO+NH₂=NH₃+NO	–9.45E–08	–9	–1.23E–08	–9	...	...
(R3) H+NO(+M)=HNO(+M)	–9.09E–08	–9	...	...	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	6.94E–08	7	8.73E–09	7	...	...
(R261) OH+CH ₂ O=HCO+H ₂ O	6.70E–08	7	9.71E–09	7	...	...
(RL352) OH+NO ₂ (+M)=HNO ₃ (+M)	...	...	1.02E–08	8	...	...
(R196) HNNO+NO=NNH+NO₂	...	...	7.03E–09	5	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(R165) NO+H=N+OH	...	...	...	...	[8.17E–08]	[11]
(R115) N ₂ O+O=NO+NO	...	...	...	...	[4.18E–08]	[5]
(R3) H+NO(+M)=HNO(+M)	[–5.19E–08]	[–3]	...	...	[4.22E–08]	[5]

^a 2nd grid point $x = 1.17 \times 10^{-9}$ cm, $T = 1434$ K.

^b 2nd grid point $x = 1.45 \times 10^{-10}$ cm, $T = 1438$ K.

^c 2nd grid point $x = 5.33 \times 10^{-10}$ cm, $T = 1418$ K.

^d Values for NG(*l*) shown.

Table B-9 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–N₂ burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	2.16E–05	100	5.94E–06	100	1.73E–06	100
(R200) HCO+NO=HNO+CO	–7.75E–06	–36	–2.64E–06	–44	–1.27E–06	–73
(R261) OH+CH ₂ O=HCO+H ₂ O	8.03E–06	37	3.51E–06	59	6.49E–07	37
(R23) HONO+OH=H ₂ O+NO ₂	–5.73E–06	–27	–2.32E–06	–39	–4.58E–07	–26
(RL776) NG=DICACOI+NO ₂	...	...	...	...	4.53E–07	26
(R94) NO ₂ +H=NO+OH	1.50E–06	7	5.48E–07	9	3.99E–07	23
(R4) NO+OH(+M)=HONO(+M)	4.70E–07	2	1.61E–06	27	3.23E–07	19
(R21) HNO+NO ₂ =HONO+NO	7.55E–07	4	5.43E–07	9	2.59E–07	15
(RL904) HCOCONO ₂ =CDOCOI+NO ₂	...	...	...	...	2.54E–07	15
(RL858) CDOCOI+COH=COHCDO+HCO	...	...	...	...	2.42E–07	14
(RL778) NG=CACACOI+NO ₂	...	...	...	...	–2.26E–07	–13
(R350) HCO+NO ₂ =CO+HONO	–1.16E–05	–54	–2.49E–06	–42	–2.09E–07	–12
(R43) CO+OH=CO ₂ +H	2.20E–07	1	2.46E–07	4	1.98E–07	11
(RL859) CDOCOI+COH=CHOCHO+CH ₂ OH	...	...	...	...	–1.81E–07	–10
(RL779) CACACOI=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	1.56E–07	9
(R161) H+HNO=H ₂ +NO	–5.20E–07	–2	–3.02E–07	–5	–1.49E–07	–9
(R160) HNO+OH=NO+H ₂ O	–3.86E–07	–2	–2.79E–07	–5	–1.27E–07	–7
(R49) OH+H ₂ =H ₂ O+H	...	...	1.74E–07	3	1.18E–07	7
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	1.12E–07	6
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	–1.65E–07	–1	...	...	1.08E–07	6
(RL632) HCOOH=HCO+OH	...	...	–4.02E–07	–7	...	...
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(R36) HCO+OH=H ₂ O+CO	[–1.91E–06]	[–5]	[–1.98E–07]	[–4]	[–1.06E–07]	[–6]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 705$ K.^b 2nd grid point $x = 3.23 \times 10^{-8}$ cm, $T = 690$ K.^c 2nd grid point $x = 1.91 \times 10^{-8}$ cm, $T = 666$ K.^d Values for NG(*I*) shown.

Table B-10 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–N₂ burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	9.51E–07	60	1.35E–07	68	7.06E–07	100
(R43) CO+OH=CO ₂ +H	6.92E–07	43	9.08E–08	46	3.05E–07	43
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.60E–06	100	2.00E–07	100	2.70E–07	38
(R186) CO+NO ₂ =NO+CO ₂	7.07E–07	44	9.26E–08	46	2.08E–07	30
(R21) HNO+NO ₂ =HONO+NO	–3.32E–07	–21	–4.60E–08	–23	–1.37E–07	–19
(R200) HCO+NO=HNO+CO	–9.03E–07	–57	–1.10E–07	–55	–1.32E–07	–19
(R160) HNO+OH=NO+H ₂ O	–2.79E–07	–18	–4.06E–08	–20	–1.27E–07	–18
(R161) H+HNO=H ₂ +NO	–2.06E–07	–13	–2.88E–08	–14	–1.19E–07	–17
(R23) HONO+OH=H ₂ O+NO ₂	–6.55E–07	–41	–9.48E–08	–48	–1.02E–07	–15
(R37) HCO+M=H+CO+M	–4.48E–07	–28	–5.98E–08	–30	–1.02E–07	–14
(RL776) NG=DICACOI+NO ₂	...	...	...	...	9.26E–08	13
(RL778) NG=CACACOI+NO ₂	...	...	...	...	–7.79E–08	–11
(RL780) CACACOI=CDOCACOI+NO ₂	...	...	...	...	6.58E–08	9
(R165) NO+H=N+OH	...	...	...	...	6.50E–08	9
(R4) NO+OH(+M)=HONO(+M)	4.35E–07	27	5.63E–08	28	6.30E–08	9
(R49) OH+H ₂ =H ₂ O+H	1.45E–07	9	2.44E–08	12	4.96E–08	7
(R116) H+HNO=NH+OH	...	...	...	...	4.74E–08	7
(RL628) CH ₂ O+OH=HCOOH+H	...	...	2.73E–08	14	4.40E–08	6
(R3) H+NO(+M)=HNO(+M)	–5.78E–08	–4	...	...	3.72E–08	5
(R170) N ₂ O+NO=N ₂ +NO ₂	7.11E–08	4	...	...	3.60E–08	5
(R261) OH+CH ₂ O=HCO+H ₂ O	4.56E–07	29	5.03E–08	25	...	...
(R349) CH ₂ O+NO ₂ =HCO+HONO	3.81E–07	24	4.74E–08	24	...	...
(R94) NO ₂ +H=NO+OH	1.59E–07	10	1.81E–08	9	...	...
(R229) H+CH ₂ O=HCO+H ₂	–1.45E–07	–9	–2.49E–08	–13	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	1.25E–07	8	1.80E–08	9	...	...
(R350) HCO+NO ₂ =CO+HONO	–8.05E–08	–5	–9.17E–09	–5	...	...
(R352) OH+NO ₂ (+M)=HNO ₃ (+M)	...	...	1.28E–08	6	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(R115) N ₂ O+O=NO+NO	...	...	...	...	[4.18E–08]	[5]

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1341$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1348$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1335$ K.

^d Values for NG(*l*) shown.

Table B-11 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–H₂CO burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	2.54E-05	100	3.68E-06	100	1.56E-06	100
(R200) HCO+NO=HNO+CO	-9.01E-06	-36	-1.69E-06	-46	-1.21E-06	-77
(R261) OH+CH ₂ O=HCO+H ₂ O	9.24E-06	36	2.17E-06	59	5.83E-07	37
(R23) HONO+OH=H ₂ O+NO ₂	-6.83E-06	-27	-1.54E-06	-42	-4.79E-07	-31
(RL776) NG=DICAC ₂ OJ+NO ₂	...	...	...	...	3.32E-07	21
(R4) NO+OH(+M)=HONO(+M)	4.56E-07	2	1.05E-06	28	3.18E-07	20
(R21) HNO+NO ₂ =HONO+NO	9.11E-07	4	3.82E-07	10	2.96E-07	19
(R94) NO ₂ +H=NO+OH	1.60E-06	6	2.97E-07	8	2.92E-07	19
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	2.43E-07	16
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	2.19E-07	14
(R350) HCO+NO ₂ =CO+HONO	-1.41E-05	-55	-1.55E-06	-42	-1.87E-07	-12
(R43) CO+OH=CO ₂ +H	2.68E-07	1	1.71E-07	5	1.86E-07	12
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	-1.81E-07	-12
(R161) H+HNO=H ₂ +NO	-6.01E-07	-2	-2.08E-07	-6	-1.73E-07	-11
(R181) H₂CO+H=NH₂+CO	1.12E-07	0	8.79E-08	2	1.56E-07	10
(R160) HNO+OH=NO+H ₂ O	-4.64E-07	-2	-2.00E-07	-5	-1.47E-07	-9
(RL778) NG=CACAC ₂ OJ+NO ₂	...	...	...	...	-1.34E-07	-9
(R49) OH+H ₂ =H ₂ O+H	...	...	1.12E-07	3	1.09E-07	7
(RL779) CACAC ₂ OJ=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	1.07E-07	7
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	-1.91E-07	-1	...	...	9.26E-08	6
(R179) H₂CO+OH=NH₂+CO₂	...	...	6.37E-08	2	8.36E-08	5
(R36) HCO+OH=H ₂ O+CO	-8.68E-07	-3	-1.38E-07	-4	-8.27E-08	-5
(R178) H₂CO+OH=H₂O+NCO	...	...	5.67E-08	2	7.44E-08	5
(R102) NCO+NO=CO₂+N₂	...	...	5.06E-08	1	6.87E-08	4
(R229) H+CH ₂ O=HCO+H ₂	-2.17E-07	-1	-1.53E-07	-4	-6.26E-08	-4
(RL632) HCOOH=HCO+OH	...	...	-2.38E-07	-6	-6.05E-08	-4
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	[1.26E-07]	[7]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 692$ K.

^b 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 679$ K.

^c 2nd grid point $x = 1.91 \times 10^{-8}$ cm, $T = 664$ K.

^d Values for NG(*I*) shown.

Table B-12 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–H₂CO burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.86E–06	100	2.71E–07	100	8.22E–07	100
(R43) CO+OH=CO ₂ +H	7.85E–07	42	1.10E–07	41	2.91E–07	35
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.28E–06	68	1.53E–07	56	2.12E–07	26
(R186) CO+NO ₂ =NO+CO ₂	6.03E–07	32	7.51E–08	28	1.70E–07	21
(R160) HNO+OH=NO+H ₂ O	–4.04E–07	–22	–5.62E–08	–21	–1.45E–07	–18
(R161) H+HNO=H ₂ +NO	–3.34E–07	–18	–4.48E–08	–17	–1.42E–07	–17
(R21) HNO+NO ₂ =HONO+NO	–3.93E–07	–21	–5.59E–08	–21	–1.39E–07	–17
(R165) NO+H=N+OH	2.18E–07	12	3.47E–08	13	1.13E–07	14
(R23) HONO+OH=H ₂ O+NO ₂	–7.36E–07	–40	–9.15E–08	–34	–1.12E–07	–14
(R200) HCO+NO=HNO+CO	–6.96E–07	–37	–8.01E–08	–30	–9.68E–08	–12
(R116) H+HNO=NH+OH	1.63E–07	9	2.54E–08	9	8.98E–08	11
(R37) HCO+M=H+CO+M	–3.79E–07	–20	–4.89E–08	–18	–8.38E–08	–10
(R181) H₂CO+H=NH₂+CO	2.26E–07	12	2.87E–08	11	7.52E–08	9
(R4) NO+OH(+M)=HONO(+M)	3.70E–07	20	3.97E–08	15	6.50E–08	8
(R179) H₂CO+OH=NH₂+CO₂	2.11E–07	11	2.69E–08	10	6.08E–08	7
(RL780) CACACOH=CDOACOH+NO ₂	...	...	...	...	5.55E–08	7
(R178) H₂CO+OH=H₂O+NCO	2.54E–07	14	2.23E–08	8	5.35E–08	7
(R147) NH₂+NO=NNH+OH	1.42E–07	8	2.09E–08	8	5.02E–08	6
(R115) N ₂ O+O=NO+NO	...	...	1.38E–08	5	4.49E–08	5
(R49) OH+H ₂ =H ₂ O+H	1.59E–07	9	2.44E–08	9	4.43E–08	5
(R170) N ₂ O+NO=N ₂ +NO ₂	1.14E–07	6	1.73E–08	6	4.29E–08	5
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	4.26E–08	5
(RL628) CH ₂ O+OH=HCOOH+H	...	...	2.51E–08	9	4.12E–08	5
(R349) CH ₂ O+NO ₂ =HCO+HONO	3.72E–07	20	3.99E–08	15	...	...
(R261) OH+CH ₂ O=HCO+H ₂ O	1.84E–07	10	...	...	...	...
(R229) H+CH ₂ O=HCO+H ₂	–1.65E–07	–9	–2.74E–08	–10	...	...
(R102) NCO+NO=CO₂+N₂	1.36E–07	7	1.57E–08	6	...	...
(R101) NCO+NO=N₂O+CO	–1.24E–07	–7	–1.62E–08	–6	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	1.14E–07	6	1.48E–08	5	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(RL776) NG=DICACOH+NO ₂	...	...	...	...	[1.03E–07]	[13]
(RL778) NG=CACACOH+NO ₂	...	...	...	...	[–8.95E–08]	[–12]
(R3) H+NO(+M)=HNO(+M)	[–5.19E–08]	[–3]	...	...	[4.22E–08]	[5]
(R94) NO ₂ +H=NO+OH	[1.77E–07]	[10]	[1.88E–08]	[9]	...	...

^a 2nd grid point $x = 1.46 \times 10^{-9}$ cm, $T = 1363$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1366$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1373$ K.

^d Values for NG(*l*) shown.

Table B-13 Normalized temperature sensitivity coefficients at the 2nd grid point: NG-CH₂O burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.66E-05	100	3.30E-06	100	1.74E-06	100
(R200) HCO+NO=HNO+CO	-6.28E-06	-38	-1.52E-06	-46	-1.32E-06	-76
(R261) OH+CH ₂ O=HCO+H ₂ O	6.05E-06	36	1.87E-06	57	6.25E-07	36
(R23) HONO+OH=H ₂ O+NO ₂	-4.48E-06	-27	-1.26E-06	-38	-4.50E-07	-26
(R94) NO ₂ +H=NO+OH	1.23E-06	7	3.70E-07	11	4.30E-07	25
(RL776) NG=DICACOI+NO ₂	...	...	...	...	4.10E-07	24
(R4) NO+OH(+M)=HONO(+M)	8.42E-07	5	1.04E-06	32	3.85E-07	22
(R21) HNO+NO ₂ =HONO+NO	7.10E-07	4	3.28E-07	10	2.58E-07	15
(RL904) HCOCONO ₂ =CDOCOI+NO ₂	...	...	...	...	2.45E-07	14
(RL858) CDOCOI+COH=COHCDO+HCO	...	...	...	...	2.27E-07	13
(R350) HCO+NO ₂ =CO+HONO	-8.99E-06	-54	-1.38E-06	-42	-2.09E-07	-12
(RL778) NG=CACACOI+NO ₂	...	...	...	...	-1.80E-07	-10
(R161) H+HNO=H ₂ +NO	-5.25E-07	-3	-2.09E-07	-6	-1.73E-07	-10
(RL859) CDOCOI+COH=CHOCHO+CH ₂ OH	...	...	...	...	-1.62E-07	-9
(R43) CO+OH=CO ₂ +H	1.85E-07	1	1.28E-07	4	1.57E-07	9
(RL779) CACACOI=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	1.39E-07	8
(R49) OH+H ₂ =H ₂ O+H	1.17E-07	1	1.09E-07	3	1.21E-07	7
(R160) HNO+OH=NO+H ₂ O	-3.44E-07	-2	-1.59E-07	-5	-1.17E-07	-7
(R36) HCO+OH=H ₂ O+CO	-5.08E-07	-3	-1.02E-07	-3	-1.06E-07	-5
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	-1.34E-07	-1	...	...	9.39E-08	5
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	8.96E-08	5
(RL632) HCOOH=HCO+OH	...	...	-1.86E-07	-6	...	...

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 684$ K.

^b 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 672$ K.

^c 2nd grid point $x = 2.38 \times 10^{-8}$ cm, $T = 653$ K.

Table B-14 Normalized temperature sensitivity coefficients at the 2nd grid point: NG-CH₂O burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.95E-06	100	2.73E-07	100	8.47E-07	100
(R43) CO+OH=CO ₂ +H	6.85E-07	35	9.27E-08	34	2.54E-07	30
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.35E-06	69	1.64E-07	60	2.21E-07	26
(R161) H+HNO=H ₂ +NO	-4.72E-07	-24	-6.28E-08	-23	-1.65E-07	-20
(R186) CO+NO ₂ =NO+CO ₂	5.14E-07	26	6.53E-08	24	1.47E-07	17
(R21) NO+NO ₂ =HONO+NO	-3.57E-07	-18	-4.90E-08	-18	-1.38E-07	-16
(R160) HNO+OH=NO+H ₂ O	-3.93E-07	-20	-5.56E-08	-20	-1.26E-07	-15
(R165) NO+H=N+OH	1.88E-07	10	2.71E-08	10	1.13E-07	13
(R200) HCO+NO=HNO+CO	-7.06E-07	-36	-8.27E-08	-30	-9.68E-08	-11
(R23) HONO+OH=H ₂ O+NO ₂	-6.57E-07	-34	-9.09E-08	-33	-9.48E-08	-11
(R116) H+HNO=NH+OH	1.49E-07	8	2.12E-08	8	8.95E-08	11
(R37) HCO+M=H+CO+M	-4.16E-07	-21	-5.40E-08	-20	-8.93E-08	-11
(R4) NO+OH(+M)=HONO(+M)	3.91E-07	20	4.92E-08	18	6.86E-08	8
(RL776) NG=DICACOJ+NO ₂	...	...	...	...	6.35E-08	8
(RL780) CACACOJ=CDOCACOH+NO ₂	...	...	...	...	6.05E-08	7
(R49) OH+H ₂ =H ₂ O+H	2.14E-07	11	3.16E-08	12	5.76E-08	7
(R3) H+NO(+M)=HNO(+M)	...	...	1.55E-08	6	5.58E-08	7
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	-5.21E-08	-6
(R229) H+CH ₂ O=HCO+H ₂	-2.39E-07	-12	-3.73E-08	-14	-4.32E-08	-5
(RL628) H ₂ O+OH=HCOOH+H	...	...	2.61E-08	10	4.30E-08	5
(R261) OH+CH ₂ O=HCO+H ₂ O	4.81E-07	25	4.93E-08	18	...	...
(R349) CH ₂ O+NO ₂ =HCO+HONO	3.88E-07	20	4.59E-08	17	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	1.65E-07	8	2.33E-08	9	...	...
(R94) NO ₂ +H=NO+OH	1.36E-07	7	1.40E-08	5	...	...
(R170) N ₂ O+NO=N ₂ +NO ₂	9.74E-08	5	...	...	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(RL778) NG=CACACOJ+NO ₂	...	...	...	...	[-8.95E-08]	[-12]
(R115) N ₂ O+O=NO+NO	...	...	...	...	[4.18E-08]	[5]

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1334$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1338$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1335$ K.

^d Values for NG(*I*) shown.

Table B-15 Normalized temperature sensitivity coefficients at the 2nd grid point: NG-urea burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO2=H+CO2+NO	1.35E-05	100	2.50E-06	100	9.14E-07	100
(R200) HCO+NO=HNO+CO	-5.17E-06	-38	-1.23E-06	-49	-7.33E-07	-80
(R23) HONO+OH=H2O+NO2	-4.17E-06	-31	-1.19E-06	-48	-3.30E-07	-36
(R261) OH+CH2O=HCO+H2O	5.09E-06	38	1.43E-06	57	3.18E-07	35
(R4) NO+OH(+M)=HONO(+M)	7.67E-07	6	8.32E-07	33	2.18E-07	24
(R94) NO2+H=NO+OH	9.00E-07	7	2.64E-07	11	2.13E-07	23
(R21) HNO+NO2=HONO+NO	7.03E-07	5	3.34E-07	13	2.00E-07	22
(RL776) NG=DICACOF+NO2	...	...	...	...	1.70E-07	19
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	1.45E-07	16
(RL904) HCOCONO2=CDOCOJ+NO2	...	...	...	...	1.23E-07	13
(R384) UREA+OH=H2NC(O)NH+H2O	2.47E-07	2	1.56E-07	6	1.15E-07	13
(R161) H+HNO=H2+NO	-4.22E-07	-3	-1.70E-07	-7	-1.10E-07	-12
(R350) HCO+NO2=CO+HONO	-7.51E-06	-56	-1.04E-06	-41	-1.08E-07	-12
(RL859) CDOCOJCOH=CHOCHO+CH2OH	...	...	...	...	-1.05E-07	-12
(R43) CO+OH=CO2+H	2.28E-07	2	1.43E-07	6	1.04E-07	11
(R160) HNO+OH=NO+H2O	-3.60E-07	-3	-1.73E-07	-7	-9.74E-08	-11
(R149) NH3+OH=NH2+H2O	1.75E-07	1	1.22E-07	5	9.38E-08	10
(RL778) NG=CACACOF+NO2	...	...	...	...	-5.69E-08	-6
(R147) NH2+NO=NNH+OH	1.20E-07	1	7.27E-08	3	5.54E-08	6
(RL779) CACACOF=HCOCONO2+CH2O+NO2	...	...	...	...	5.30E-08	6
(R227) H+CH2O(+M)=CH2OH(+M)	...	...	...	...	5.10E-08	6
(R49) OH+H2=H2O+H	9.50E-08	1	7.63E-08	3	4.86E-08	5
(RL632) HCOOH=HCO+OH	...	...	-1.45E-07	-6	...	...
(R349) CH2O+NO2=HCO+HONO	2.59E-07	2	1.36E-07	5	...	...
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(R353) CHOCHO+OH=H2O+CO+HCO	...	...	...	...	[1.26E-07]	[7]
(R227) H+CH2O(+M)=CH2OH(+M)	[-3.22E-07]	[-1]	...	...	[1.24E-07]	[6]
(R36) HCO+OH=H2O+CO	[-1.91E-06]	[-5]	[-1.98E-07]	[-4]	[-1.06E-07]	[-6]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 667$ K.

^b 2nd grid point $x = 2.27 \times 10^{-8}$ cm, $T = 658$ K.

^c 2nd grid point $x = 1.43 \times 10^{-8}$ cm, $T = 649$ K.

^d Values for NG(I) shown.

Table B-16 Normalized temperature sensitivity coefficients at the 2nd grid point: NG-urea burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N2O+OH	2.16E-06	100	3.27E-07	100	9.97E-07	100
(R43) CO+OH=CO2+H	7.33E-07	34	1.08E-07	33	3.12E-07	31
(R351) HCO+NO2=H+CO2+NO	1.19E-06	55	1.45E-07	44	2.40E-07	24
(R186) CO+NO2=NO+CO2	5.38E-07	25	6.92E-08	21	1.82E-07	18
(R161) H+HNO=H2+NO	-4.08E-07	-19	-5.72E-08	-18	-1.79E-07	-18
(R160) HNO+OH=NO+H2O	-4.36E-07	-20	-6.33E-08	-19	-1.65E-07	-17
(R21) HNO+NO2=HONO+NO	-3.84E-07	-18	-5.56E-08	-17	-1.55E-07	-16
(R23) HONO+OH=H2O+NO2	-7.13E-07	-33	-9.34E-08	-29	-1.30E-07	-13
(R165) NO+H=N+OH	2.27E-07	11	3.86E-08	12	1.21E-07	12
(R200) HCO+NO=HNO+CO	-6.42E-07	-30	-7.41E-08	-23	-1.08E-07	-11
(R116) H+HNO=NH+OH	1.85E-07	9	3.03E-08	9	1.03E-07	10
(R37) HCO+M=H+CO+M	-3.52E-07	-16	-4.61E-08	-14	-9.53E-08	-10
(R147) NH2+NO=NNH+OH	2.72E-07	13	4.41E-08	14	9.16E-08	9
(R4) NO+OH(+M)=HONO(+M)	3.41E-07	16	3.73E-08	11	7.81E-08	8
(R384) UREA+OH= H2NC(O)NH +H2O	2.49E-07	12	2.88E-08	9	6.24E-08	6
(RL780) CACACOH=CDOCACOH+NO2	...	...	...	...	6.24E-08	6
(R49) OH+H2=H2O+H	1.54E-07	7	2.34E-08	7	4.86E-08	5
(R115) N2O+O=NO+NO	...	...	...	...	4.78E-08	5
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	4.67E-08	5
(R3) H+NO(+M)=HNO(+M)	...	...	...	...	4.66E-08	5
(R349) CH2O+NO2=HCO+HONO	3.57E-07	17	3.99E-08	12	...	...
(R261) OH+CH2O=HCO+H2O	1.60E-07	7	...	...	...	...
(R229) H+CH2O=HCO+H2	-1.59E-07	-7	-2.70E-08	-8	...	...
(R195) HNO+NO+NO=HNNO+NO2	1.36E-07	6	1.94E-08	6	...	...
(R149) NH3+OH=NH2+H2O	1.18E-07	5	...	...	...	...
(R170) N2O+NO=N2+NO2	1.13E-07	5	1.72E-08	5	...	...
(RL628) CH2O+OH=HCOOH+H	...	...	2.27E-08	7	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(RL776) NG=DICACOH+NO2	...	...	...	...	[1.03E-07]	[13]
(RL778) NG=CACACOH+NO2	...	...	...	...	-8.95E-08]	[-12]
(RL628) CH2O+OH=HCOOH+H	...	...	[3.10E-08]	[15]	[5.08E-08]	[7]

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1330$ K.

^b 2nd grid point $x = 1.96 \times 10^{-10}$ cm, $T = 1333$ K.

^c 2nd grid point $x = 4.47 \times 10^{-10}$ cm, $T = 1340$ K.

^d Values for NG(*l*) shown.

Table B-17 Normalized temperature sensitivity coefficients at the 2nd grid point: NG-urea-spv2 burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO2=H+CO2+NO	1.22E-05	100	2.55E-06	100	1.21E-06	100
(R200) HCO+NO=HNO+CO	-5.00E-06	-41	-1.28E-06	-50	-9.54E-07	-79
(R261) OH+CH2O=HCO+H2O	4.69E-06	38	1.47E-06	58	4.17E-07	35
(R23) HONO+OH=H2O+NO2	-4.17E-06	-34	-1.21E-06	-48	-4.08E-07	-34
(R4) NO+OH(+M)=HONO(+M)	1.12E-06	9	8.88E-07	35	2.79E-07	23
(R94) NO2+H=NO+OH	8.71E-07	7	2.79E-07	11	2.74E-07	23
(RL776) NG=DICACOJ+NO2	...	...	...	...	2.46E-07	20
(R21) HNO+NO2=HONO+NO	8.37E-07	7	3.31E-07	13	2.26E-07	19
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	1.74E-07	14
(R149) NH3+OH=NH2+H2O	6.98E-07	6	2.03E-07	8	1.60E-07	13
(R43) CO+OH=CO2+H	2.55E-07	2	1.71E-07	7	1.56E-07	13
(RL904) HCOCONO2=CDOCOJ+NO2	...	...	...	...	1.57E-07	13
(R350) HCO+NO2=CO+HONO	-6.51E-06	-53	-1.02E-06	-40	-1.41E-07	-12
(R161) H+HNO=H2+NO	-4.86E-07	-4	-1.74E-07	-7	-1.28E-07	-11
(RL859) CDOCOJCOH=CHOCHO+CH2OH	...	...	...	...	-1.24E-07	-10
(R160) HNO+OH=NO+H2O	-4.25E-07	-3	-1.77E-07	-7	-1.13E-07	-9
(RL778) NG=CACACOJ+NO2	...	...	...	...	-1.00E-07	-8
(RL779) CACACOJ=HCOCONO2+CH2O+NO2	...	...	...	...	8.18E-08	7
(R49) OH+H2=H2O+H	1.12E-07	1	8.95E-08	4	7.39E-08	6
(R227) H+CH2O(+M)=CH2OH(+M)	...	...	...	...	6.83E-08	6
(RL632) HCOOH=HCO+OH	...	...	-1.36E-07	-5	...	...
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(R353) CHOCHO+OH=H2O+CO+HCO	...	...	...	...	[1.26E-07]	[7]
(R36) HCO+OH=H2O+CO	[-1.91E-06]	[-5]	[-1.98E-07]	[-4]	[-1.06E-07]	[-6]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 666$ K.

^b 2nd grid point $x = 2.43 \times 10^{-8}$ cm, $T = 653$ K.

^c 2nd grid point $x = 1.91 \times 10^{-8}$ cm, $T = 644$ K.

^d Values for NG(*l*) shown.

Table B-18 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–urea–spv2 burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.99E–06	100	2.92E–07	100	1.00E–06	100
(R43) CO+OH=CO ₂ +H	6.90E–07	35	1.09E–07	37	3.45E–07	34
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.18E–06	60	1.72E–07	59	2.56E–07	25
(R186) CO+NO ₂ =NO+CO ₂	5.24E–07	26	7.80E–08	27	2.01E–07	20
(R161) H+HNO=H ₂ +NO	–3.95E–07	–20	–5.07E–08	–17	–1.66E–07	–17
(R160) HNO+OH=NO+H ₂ O	–4.23E–07	–21	–5.96E–08	–20	–1.64E–07	–16
(R21) HNO+NO ₂ =HONO+NO	–3.57E–07	–18	–5.50E–08	–19	–1.60E–07	–16
(R165) NO+H=N+OH	1.83E–07	9	3.10E–08	11	1.26E–07	13
(R23) HONO+OH=H ₂ O+NO ₂	–7.96E–07	–40	–9.59E–08	–33	–1.23E–07	–12
(R200) HCO+NO=HNO+CO	–6.48E–07	–33	–9.37E–08	–32	–1.19E–07	–12
(R37) HCO+M=H+CO+M	–3.38E–07	–17	–5.10E–08	–17	–9.85E–08	–10
(R116) H+HNO=NH+OH	1.54E–07	8	2.19E–08	7	9.53E–08	9
(R4) NO+OH(+M)=HONO(+M)	4.15E–07	21	3.91E–08	13	7.18E–08	7
(RL780) CACAC ₂ OJ=CDOCAC ₂ OH+NO ₂	...	...	...	...	6.36E–08	6
(R115) N ₂ O+O=NO+NO	...	...	...	...	5.60E–08	6
(RL776) NG=DICAC ₂ OJ+NO ₂	...	...	...	...	5.56E–08	6
(R49) OH+H ₂ =H ₂ O+H	1.47E–07	7	2.78E–08	10	5.32E–08	5
(R3) H+NO(+M)=HNO(+M)	...	...	...	...	4.97E–08	5
(R149) NH₃+OH=NH₂+H₂O	4.54E–07	23	2.97E–08	10	4.79E–08	5
(RL628) CH ₂ O+OH=HCOOH+H	...	...	2.27E–08	8	4.61E–08	5
(R349) CH ₂ O+NO ₂ =HCO+HONO	3.90E–07	20	4.41E–08	15	...	...
(R147) NH₂+NO=NNH+OH	2.69E–07	14	1.97E–08	7	...	...
(R229) H+CH ₂ O=HCO+H ₂	–1.59E–07	–8	–3.02E–08	–10	...	...
(R170) N ₂ O+NO=N ₂ +NO ₂	1.13E–07	6	1.61E–08	5	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	1.27E–07	6	1.96E–08	7	...	...
(R261) OH+CH ₂ O=HCO+H ₂ O	1.19E–07	6	1.92E–08	7	...	...
(R178) HNCO+OH=H₂O+NCO	1.16E–07	6	...	...	...	...
(R181) HNCO+H=NH₂+CO	1.14E–07	6	...	...	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(RL778) NG=CACAC ₂ OJ+NO ₂	...	...	...	...	[–8.95E–08]	[–12]

^a 2nd grid point $x = 1.49 \times 10^{-9}$ cm, $T = 1335$ K.

^b 2nd grid point $x = 2.04 \times 10^{-10}$ cm, $T = 1323$ K.

^c 2nd grid point $x = 4.47 \times 10^{-10}$ cm, $T = 1327$ K.

^d Values for NG(*l*) shown.

Table B-19 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–NH₃–HNCO burning at 10 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R351) HCO+NO ₂ =H+CO ₂ +NO	4.29E–05	100	5.28E–06	100	2.85E–06	100
(R200) HCO+NO=HNO+CO	–1.62E–05	–38	–2.45E–06	–46	–2.19E–06	–77
(R261) OH+CH ₂ O=HCO+H ₂ O	1.62E–05	38	2.98E–06	56	9.90E–07	35
(R23) HONO+OH=H ₂ O+NO ₂	–1.25E–05	–29	–2.31E–06	–44	–9.10E–07	–32
(R94) NO ₂ +H=NO+OH	3.17E–06	7	5.16E–07	10	7.08E–07	25
(R21) HNO+NO ₂ =HONO+NO	2.12E–06	5	6.64E–07	13	6.68E–07	24
(R149) NH₃+OH=NH₂+H₂O	1.13E–06	3	5.34E–07	10	6.44E–07	23
(R4) NO+OH(+M)=HONO(+M)	2.04E–06	5	1.54E–06	29	6.10E–07	21
(RL776) NG=DICACOF+NO ₂	...	...	...	...	5.74E–07	20
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	5.17E–07	18
(RL904) HCOCONO ₂ =CDOCOJ+NO ₂	...	...	...	...	4.39E–07	15
(RL859) CDOCOJCOH=CHOCHO+CH ₂ OH	...	...	...	...	–4.03E–07	–14
(R161) H+HNO=H ₂ +NO	–1.31E–06	–3	–3.29E–07	–6	–3.50E–07	–12
(R350) HCO+NO ₂ =CO+HONO	–2.24E–05	–52	–2.15E–06	–41	–3.20E–07	–11
(R160) HNO+OH=NO+H ₂ O	–1.03E–06	–2	–3.12E–07	–6	–3.02E–07	–11
(R43) CO+OH=CO ₂ +H	4.91E–07	1	1.99E–07	4	2.70E–07	9
(R147) NH₂+NO=NNH+OH	4.54E–07	1	1.80E–07	3	2.20E–07	8
(R36) HCO+OH=H ₂ O+CO	–1.80E–06	–4	–2.43E–07	–5	–2.00E–07	–7
(R37) HCO+M=H+CO+M	6.14E–07	1	2.07E–07	4	1.91E–07	7
(R227) H+CH ₂ O(+M)=CH ₂ OH(+M)	–3.13E–07	–1	...	...	1.84E–07	6
(RL778) NG=CACACOF+NO ₂	...	...	...	...	–1.83E–07	–6
(R49) OH+H ₂ =H ₂ O+H	2.64E–07	1	1.49E–07	3	1.73E–07	6
(RL632) HCOOH=HCO+OH	...	...	–4.18E–07	–8	–1.70E–07	–6
(R181) HNCO+H=NH₂+CO	...	...	6.34E–08	1	1.57E–07	6
(R229) H+CH ₂ O=HCO+H ₂	–4.46E–07	–1	–2.25E–07	–4	–1.12E–07	–4
(R162) HNO+NH₂=NH₃+NO	...	...	–7.48E–08	–1	–8.31E–08	–3
(R179) HNCO+OH=NH₂+CO₂	...	...	4.15E–08	1	7.28E–08	3
(R349) CH ₂ O+NO ₂ =HCO+HONO	6.70E–07	2	2.49E–07	5	6.59E–08	2
(R102) NCO+NO=CO₂+N₂	...	...	3.44E–08	1	6.26E–08	2
(R178) HNCO+OH=H₂O+NCO	...	...	3.21E–08	1	5.84E–08	2
Reactions in Table B-1 that are not listed above ^d	...	...	...	...	...	...
(RL779) CACACOF=HCOCONO ₂ +CH ₂ O+NO ₂	...	...	...	...	[1.72E–07]	[9]
(R353) CHOCHO+OH=H ₂ O+CO+HCO	...	...	...	...	[1.26E–07]	[7]

^a 2nd grid point $x = 7.81 \times 10^{-8}$ cm, $T = 705$ K.

^b 2nd grid point $x = 3.08 \times 10^{-8}$ cm, $T = 692$ K.

^c 2nd grid point $x = 3.25 \times 10^{-8}$ cm, $T = 676$ K.

^d Values for NG(*I*) shown.

Table B-20 Normalized temperature sensitivity coefficients at the 2nd grid point: NG–NH₃–HNCO burning at 2000 atm

Reaction	DZ/NPS-1 ^a		PM/NPS-1 ^b		PM/NPS-2 ^c	
	absolute	relative	absolute	relative	absolute	relative
(R19) HNO+NO=N ₂ O+OH	1.20E–06	100	1.98E–07	100	7.47E–07	100
(R43) CO+OH=CO ₂ +H	5.30E–07	44	7.93E–08	40	2.55E–07	34
(R351) HCO+NO ₂ =H+CO ₂ +NO	1.19E–06	99	1.61E–07	81	2.29E–07	31
(R186) CO+NO ₂ =NO+CO ₂	5.23E–07	44	7.45E–08	38	1.75E–07	23
(R161) H+HNO=H ₂ +NO	–2.94E–07	–25	–4.50E–08	–23	–1.51E–07	–20
(R160) HNO+OH=NO+H ₂ O	–3.41E–07	–28	–5.32E–08	–27	–1.43E–07	–19
(R23) HONO+OH=H ₂ O+NO ₂	–8.43E–07	–70	–1.20E–07	–61	–1.41E–07	–19
(R21) HNO+NO ₂ =HONO+NO	–2.77E–07	–23	–4.36E–08	–22	–1.25E–07	–17
(R149) NH₃+OH=NH₂+H₂O	5.24E–07	44	7.27E–08	37	1.03E–07	14
(R200) HCO+NO=HNO+CO	–6.32E–07	–53	–8.20E–08	–42	–1.02E–07	–14
(R37) HCO+M=H+CO+M	–3.62E–07	–30	–5.25E–08	–27	–9.18E–08	–12
(R4) NO+OH(+M)=HONO(+M)	5.29E–07	44	6.70E–08	34	9.14E–08	12
(R147) NH₂+NO=NNH+OH	2.31E–07	19	3.90E–08	20	8.33E–08	11
(RL780) CACAC ₂ OJ=CDOAC ₂ OH+NO ₂	...	...	...	...	7.11E–08	10
(RL776) NG=DICAC ₂ OJ+NO ₂	...	...	...	...	6.93E–08	9
(R165) NO+H=N+OH	...	...	...	...	6.72E–08	9
(R116) H+HNO=NH+OH	...	...	1.01E–08	5	6.59E–08	9
(RL778) NG=CACAC ₂ OJ+NO ₂	...	...	...	...	–5.87E–08	–8
(RL858) CDOCOJCOH=COHCDO+HCO	...	...	...	...	4.61E–08	6
(R349) CH ₂ O+NO ₂ =HCO+HONO	4.14E–07	35	5.33E–08	27	4.46E–08	6
(R178) HNCO+OH=H₂O+NCO	1.35E–07	11	1.63E–08	8	4.44E–08	6
(RL628) CH ₂ O+OH=HCOOH+H	...	...	2.52E–08	13	4.34E–08	6
(R49) OH+H ₂ =H ₂ O+H	1.26E–07	11	2.10E–08	11	4.20E–08	6
(R170) N ₂ O+NO=N ₂ +NO ₂	8.80E–08	7	1.39E–08	7	4.00E–08	5
(R261) OH+CH ₂ O=HCO+H ₂ O	1.49E–07	12	1.50E–08	8	...	...
(R229) H+CH ₂ O=HCO+H ₂	–1.47E–07	–12	–2.62E–08	–13	...	...
(R94) NO ₂ +H=NO+OH	1.44E–07	12	1.64E–08	8	...	...
(R181) HNCO+H=NH₂+CO	1.19E–07	10	...	...	...	...
(R179) HNCO+OH=NH₂+CO₂	1.04E–07	9	1.42E–08	7	...	...
(R195) HNO+NO+NO=HNNO+NO ₂	9.44E–08	8	1.36E–08	7	...	...
(R3) H+NO(+M)=HNO(+M)	–8.53E–08	–7	...	...	...	...
(R102) NCO+NO=CO₂+N₂	8.10E–08	7	1.02E–08	5	...	...
(RL352) OH+NO ₂ (+M)=HNO ₃ (+M)	...	...	1.09E–08	6	...	...
Reactions in Table B-2 that are not listed above ^d	...	...	...	...	...	...
(R3) H+NO(+M)=HNO(+M)	[–5.19E–08]	[–3]	...	...	[4.22E–08]	[5]
(R115) N ₂ O+O=NO+NO	...	...	...	...	[4.18E–08]	[5]

^a 2nd grid point $x = 1.33 \times 10^{-9}$ cm, $T = 1392$ K.

^b 2nd grid point $x = 1.86 \times 10^{-10}$ cm, $T = 1397$ K.

^c 2nd grid point $x = 3.73 \times 10^{-10}$ cm, $T = 1393$ K.

^d Values for NG(*l*) shown.

**Appendix C. Pathway Diagrams for the Consumption of
Prominent Species near the Surface of NG–NH₃, NG–HNCO,
and NG–Urea Burning at 10 atm**

Appendix C presents graphical depictions of pathway-specific rates by which prominent species were consumed via chemical reactions at the 2nd grid point of solutions for the burning of NG-NH₃, NG-HNCO, and NG-urea at 10 atm. The diagrams are based on results produced by the PM/NPS-2 model. Arrows indicate reactant-product connections. The widths of the arrows are proportional to the molar consumption rate of the reactant (species) in the box at the arrow's tail. Species listed next to the arrows are co-reactants, and the numbers associated with them indicate the consumption rate of the reactant in the box due to its reaction with the co-reactant relative to the rate of all other reactions at that spatial location. Absolute rates are scaled to a range in which the value for the largest molar consumption rate produced by any reaction at the location is 100. To reduce clutter, reactions that produced molar consumption rates less than 5% of the maximum individual rate at the given location are not shown. (Moreover, they do not contribute to an arrow's width.) For these three mixtures, no pathways for the consumption of the additive's parent molecule had a rate that reached 5% of the individual maximum at the location. That is why none are observed.

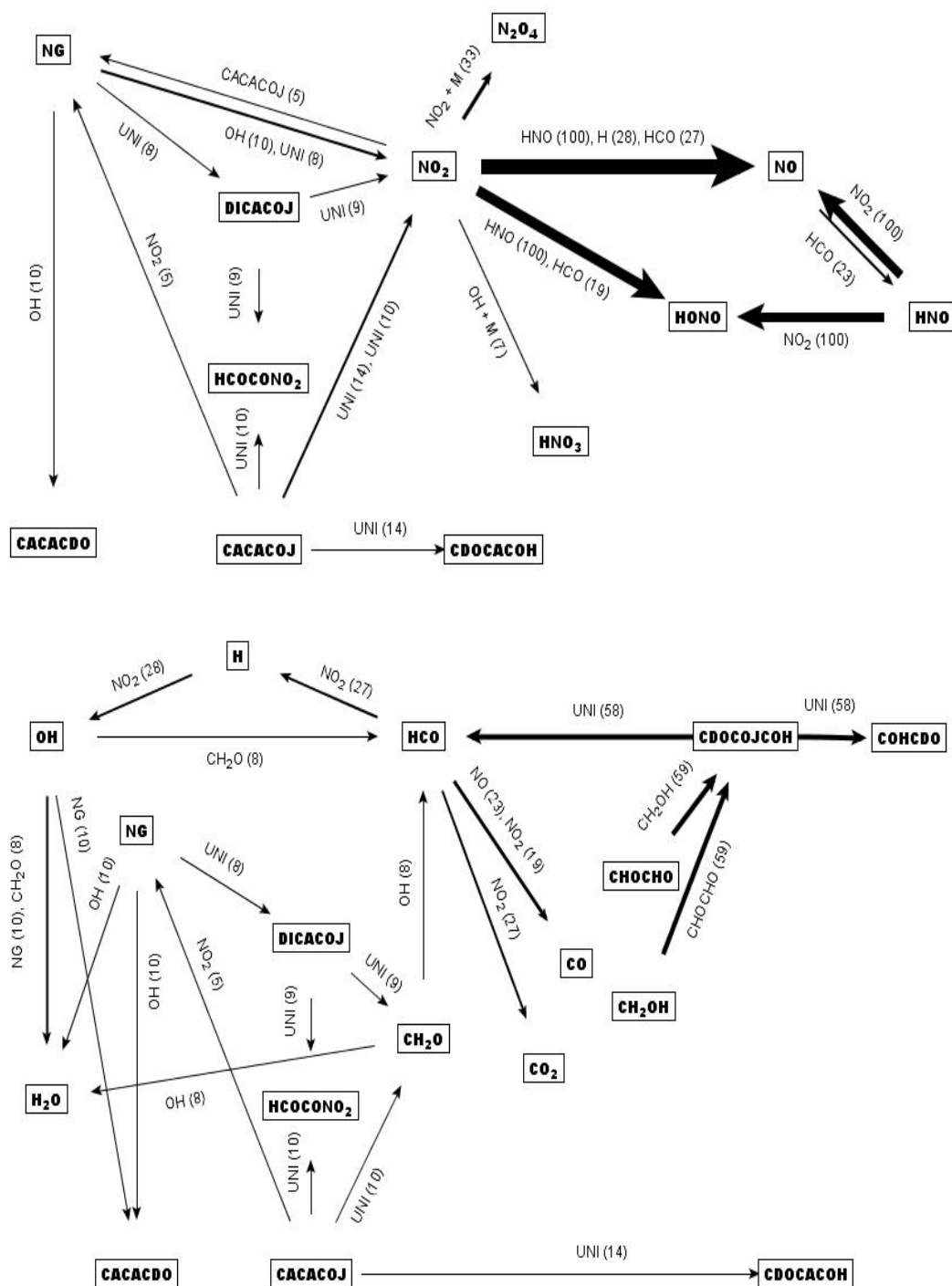


Fig. C-1 Pathway diagrams of species consumption for NG-NH₃ burning at 10 atm; PM/NPS-2 results at the 2nd grid point: $x = 2.84 \times 10^{-8}$ cm, $T = 687$ K

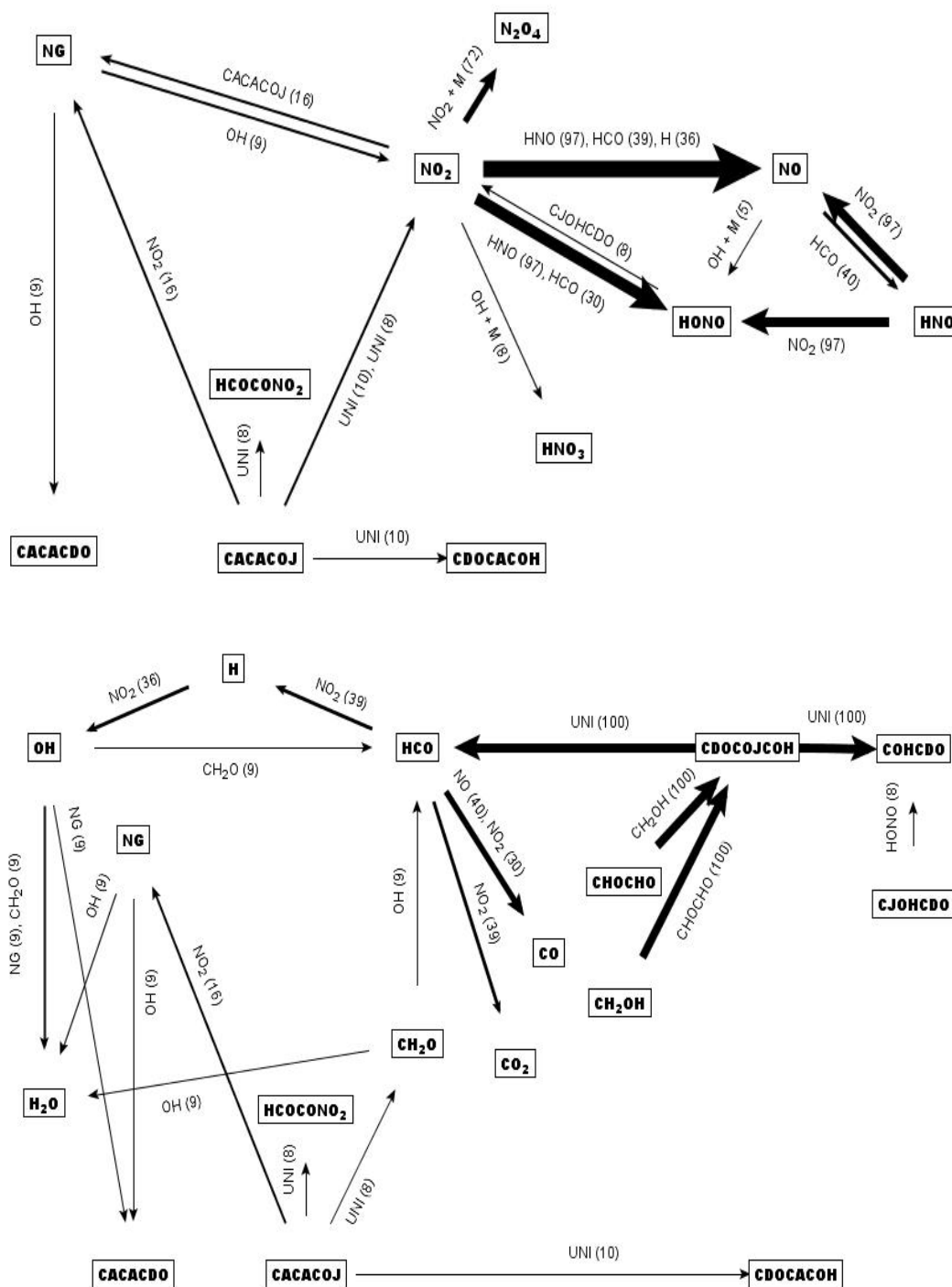


Fig. C-3 Pathway diagrams of species consumption for NG-urea burning at 10 atm; PM/NPS-2 results at the 2nd grid point: $x = 1.43 \times 10^{-8}$ cm, $T = 649$ K

List of Symbols, Abbreviations, and Acronyms

1-D	one-dimensional
C ₂ H ₅ O	ethoxide
C ₂ H ₅ OH	ethanol
CH ₂ O	formaldehyde
CH ₃ O	methoxide
CH ₃ OH	methanol
d_{DZ}	dark zone length
DZ	(“dark zone”) mechanism
EM	energetic material
H ₂	hydrogen
HCO	formyl radical
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazoctane
HN ₃	hydrazoic acid
HNCO	isocyanic acid
HNO	nitroxyl
HONO	nitrous acid
kcal/mol	kilocalories per mole
MMH	monomethylhydrazine
N ₂	nitrogen
N ₂ H ₄	hydrazine
N ₂ O	nitrous oxide
N ₃	azide
NC	nitrocellulose
NG	nitroglycerin
NG(g)	gaseous nitroglycerin
NG(l)	liquid nitroglycerin
NH	imidogen
NH ₂	amino radical

NH ₃	ammonia
NO	nitric oxide
NO ₂	nitrogen dioxide
NO _x	nitrogen oxides
NPS	nascent product set
NQ	nitroguanidine
N _x H _y	nitrogen hydrides
OH	hydroxyl radical
<i>P</i>	pressure
PM	("parent molecule") mechanism
QM	quantum mechanics
RDX	1,3,5-trinitro-1,3,5-triazacyclohexane
RFNA	red fuming nitric acid
spv2	surface product variation 2
STMBMS	simultaneous thermogravimetric modulated beam mass spectrometer
TAGzT	triammonium guanidium tetrazolate

Notational Conventions

$\dot{\omega}_k$	species molar conversion rates
$h_c^{-\infty}$	condensed-phase enthalpy
h_g^k	gas-phase species enthalpy
$E_{a,i}$	constant in rate coefficient expression
$\dot{M}$	mass flow rate
W_k	species molecular weight
Y_g^k	gas-phase species mass fraction
$c_{p,g}$	heat capacity
k_i	reaction rate coefficient
$\dot{m}$	mass flux
n_i	constant in rate coefficient expression
$\dot{q}$	(rate of) heat release
v_g	gas-phase convective velocity
λ_g	thermal conductivity
ρ_c	condensed-phase density
τ_{DZ}	dark zone temporal parameter
$v_{ki}'' (v_{ki}')^{\prime\prime}$	the stoichiometric coefficients for i 's products (reactants)
A_i	constant in rate coefficient expression
A_c	area of the inlet
A_s	pyrolysis law constant
E_s	pyrolysis law constant
i	reaction index
I_m	impetus
I_{sp}	specific impulse
k	species index
r	burning/regression rate
R_i	molar reaction rate

R_u	universal gas constant
S_i	normalized temperature sensitivity coefficient
T	temperature
T_{AD}	adiabatic flame temperature
T_m	maximum temperature in the computational domain
x	spatial dimension
ΔH_r	enthalpy of reaction
κ_a	kinetic activity

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