



Detailed Combustion Modeling as an Aid to Propellant Formulation: Two New Strategies

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Abstract

There has been considerable progress recently in the development and use of elementary chemical-reaction mechanisms to describe the gas-phase energy release of energetic materials. Such advances present an opportunity to examine the extent to which these models might be used to provide guidance to the propellant formulator. In this report, we develop two methodologies that may prove helpful to the development of propellant formulations with tailored combustion characteristics. First, the dependence of the burning rate on the path of condensed-phase decomposition was computed for nitroglycerine (NG) combustion. It was found that some sets of decomposition products lead to nearly an order of magnitude higher burning rate than is observed experimentally. This indicates that efforts to influence the path of decomposition might be a novel and powerful approach to tailoring burning rate. Second, a methodology for calculating the effectiveness of different chemical additives on the burning rate was developed and demonstrated for several chemical additives added to NG. Burning rates were calculated for the additives H_2 , CH_2O , and NH_3 and flame-structure calculations made for HNCO as an additive. NH_3 accelerates the burning rate of NG, and HNCO is expected to retard it; both reduce the dark-zone length and thus may reduce ignition delays in guns.

Table of Contents

	<u>Page</u>
List of Figures	v
List of Tables	vii
1. Introduction	1
2. Burning-Rate Model	1
3. Effect of Condensed-Phase Decomposition Path on Burning Rate	4
4. Effects of Chemical Additives	7
5. Speculations on Practical Burning-Rate Modifiers.....	15
6. Conclusions	16
7. References	17
Appendix: Gas-Phase Reaction Mechanism	19
Distribution List	29
Report Documentation Page	37

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List of Figures

<u>Figure</u>	<u>Page</u>
1. Universal Pyrolysis Law for Double-Base Propellants Developed by Zenin	3
2. Levy's Rationalization for NG Decomposition Scheme.....	5
3. Calculated Burning Rates Based on the Assumption of Alternative Condensed-Phase Decomposition Paths	6
4. Computed Effect on Heat Feedback of Various Additive Species Combined With Levy Decomposition Products of NG at 10 atm	9

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List of Tables

<u>Table</u>	<u>Page</u>
1. Hypothetical Condensed-Phase Decomposition Pathways for NG.....	5
2. Heats of Reaction for Condensed-Phase Decomposition Sets	7
3. Effect of Different Chemical Additives on the Burning Rate of NG at 10 atm.....	11

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1. Introduction

The application of complex networks of elementary chemical reactions to the gas phase of burning energetic materials has increased markedly over the last decade [1–6]. The direction of this work raises the possibility that such chemically specific descriptions might help propellant formulators rationalize their work in a way that has long been hoped for. This report demonstrates two specific approaches that might prove useful in guiding propellant-formulation activities. The first approach involves determining how alternative condensed-phase decomposition paths might influence the burning rate by providing different sets of decomposition products that subsequently become the reactants for the gas phase. The second approach establishes a systematic method for testing the effect of specific chemical additives on the burning rate of an energetic material. This method permits the evaluation of the relative effectiveness of different additives in boosting or retarding the burning rate of an energetic material by computing the amount of each additive necessary to bring the mixture to the same oxygen balance. We believe that these calculations are the first of their kind.

2. Burning-Rate Model

For purposes of this study, we have developed a new burning-rate model that is applied to the steady-state combustion of nitroglycerine (NG) as a function of pressure. This model is predicated on the use of the following Arrhenius-like expression relating the mass burning rate to the surface temperature; this relationship is known as the “pyrolysis law” in the propellant-combustion literature [7]:

$$\dot{m} = A_s e^{-E_s/RT_s}, \quad (1)$$

where E_s is the activation energy, R is the universal gas constant, and T_s is the surface temperature. Here, the pyrolysis law is written in terms of the mass burning rate or mass flux $\dot{m}$; it could as well be expressed in terms of the linear burning rate $r = \dot{m}/\rho$, where ρ is the mass density of the unreacted solid. This expression provides the rate at which condensed-phase

molecules are converted to the gas phase. One also needs to know the chemical identities and mole fractions of these first gas-phase molecules. This information is embodied in an assumed overall chemical reaction to be discussed subsequently.

With the identity of the nascent gas-phase reactants established by the overall reaction and at a rate of appearance at the surface given by the pyrolysis law, the heat feedback to the surface can be computed using a gas-phase elementary-reaction mechanism. For this purpose, we have adapted the PREMIX code, version 2.55, developed by Kee et al. [8]. The burning rate is then found by an iterative method to satisfy the energy-flux boundary condition at the burning surface. This boundary condition is (assuming no condensed-phase molecular diffusion)

$$\lambda_c \left(\frac{dT}{dx} \right)^{-0} - \sum_i \dot{m} Y_i^{-0} h_i^{-0} = \lambda_g \left(\frac{dT}{dx} \right)^{+0} - \sum_i \dot{m} Y_i^{+0} h_i^{+0} + \sum_i \rho_g Y_i^{+0} V_i^{+0} h_i^{+0}. \quad (2)$$

In this equation, λ_c is the condensed-phase thermal conductivity, Y_i^{-0} is the mass fraction of species i on the liquid side of the surface, and h_i^{-0} is the i th species enthalpy on the liquid side of the surface. The right side of the equation contains the analogous quantities for the positive side of the surface (i.e., in the gas phase), with the addition of the diffusion velocity at the surface, V_i^{+0} , and the gas-phase mass density ρ_g . By further assuming there are no bulk-liquid reactions, one can combine the species boundary conditions with an integral over the energy conservation equation in the condensed phase over the interval $(-\infty, -0)$ to obtain the following form of the energy boundary condition at the interface between the gas and condensed phases:

$$\lambda_g \left(\frac{dT}{dx} \right)^{+0} = \dot{m} \sum_i (Y_i^{-0} h_i^{+0} - Y_i^{-\infty} h_i^{-\infty}). \quad (3)$$

Here, $-\infty$ denotes the unreacted material at its initial temperature. This form of the boundary condition is very useful because one need not know the thermophysical properties of the condensed phase at any temperature other than the initial temperature, at least for purposes of finding the burning-rate eigenvalue. Of course, if the temperature profile in the condensed phase

is desired, one must know these properties at all temperatures between the initial temperature and the surface temperature.

The concepts under discussion in this paper are illustrated using NG as the subject energetic material. For this case we use the pyrolysis law developed by Zenin [9] from his microthermocouple measurements of the surface temperature of double-base propellants ($A_s = 1.8 \times 10^3 \text{ g/cm}^2\text{-s}$, $E_s = 5,000\text{-R}$). Double-base propellants contain various proportions of nitrocellulose (NC) and NG, and, though the validity of the double-base pyrolysis law for pure NG is unproved, it is not unreasonable to suppose that the limiting step in the decomposition of NG, like that of NC, is the scission of an NO_2 group and would therefore have at least a similar activation energy as in the NC case. This may in fact account for the apparent universality of Zenin's pyrolysis law for different ingredient proportions. In Figure 1, the good quality of fit of this pyrolysis law to the data is evident.

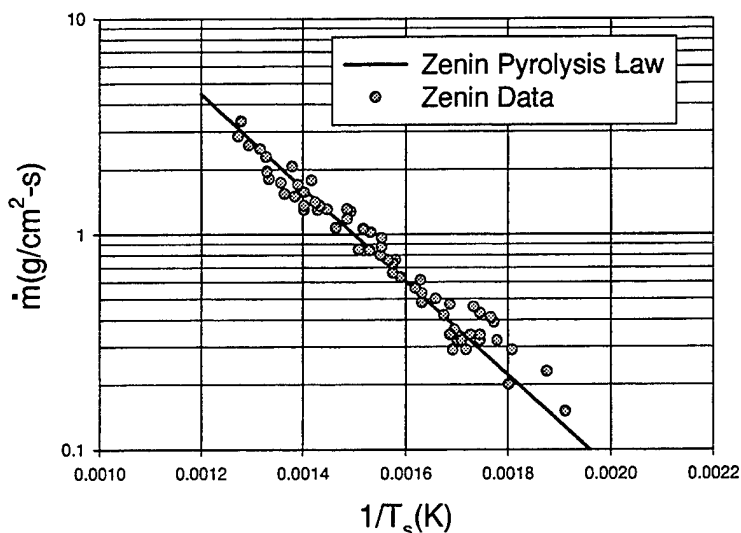


Figure 1. Universal Pyrolysis Law for Double-Base Propellants Developed by Zenin [9].

Finally, one needs to have an elementary reaction mechanism suitable for the gas-phase chemistry of NG. Our starting point here was the mechanism [10] previously developed for the dark zones of both double-base and nitramine propellants. To this mechanism, CH_2O and its associated reactions were added and HCN and its associated reactions were removed. This mechanism, referred to here as DB2, consists of 35 species and 177 reactions. For the purpose of

faster calculations, an abbreviated version, labeled DBQ1, consisting of only 19 species and 40 reactions was assembled based on experience and intuition only and not a systematic reduction method. A more systematic reduction was planned if later found to be warranted. These reaction mechanisms are given in the Appendix.

3. Effect of Condensed-Phase Decomposition Path on Burning Rate

The condensed-phase decomposition of an energetic material would, in general, be expected to be a complex chemical event, possibly involving competing parallel and sequential kinetic paths. Owing to the difficulty of measuring these events in the condensed phase, they are not known with reliability for any energetic material. In the face of this intractability, we have decided to turn the issue around and ask not what species actually result from the condensed-phase decomposition of NG, but what the effect on burning rate would be if one could influence the decomposition to occur along alternative overall-reaction paths. This approach, in fact, may be more pertinent to the issue of tailoring the burning rate to specific desired behavior; although, of course, it begs the question of how to accomplish this feat of chemical persuasion.

There have been previous attempts at discerning the overall condensed-phase decomposition path of NG. Hatch [1] chose a path for his model of NG combustion, though without rationalization. Levy [11] speculated on a sequence of reactions leading to an overall path (Figure 2). We have added a number of balanced-chemical-reaction alternatives for purposes of this study, labeled MSM1, etc. All of these possible overall reactions are collected in Table 1. No claim is made that this list is exhaustive.

The results of burning-rate calculations using the different sets of decomposition products in Table 1 and the DBQ1 reaction mechanism are shown in Figure 3. It is seen that the Levy decomposition products give excellent agreement with the experimental data over almost 4 orders of magnitude in pressure. It should be mentioned here that subsequent calculations with the more complete reaction mechanism DB2 showed that the DBQ1-calculated burning rates were about a factor of 2 too high; thus, the MSM4 decomposition set gives the best

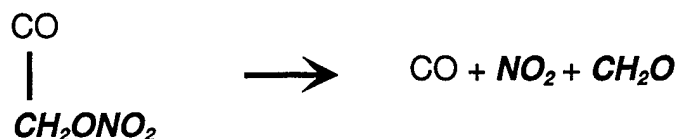
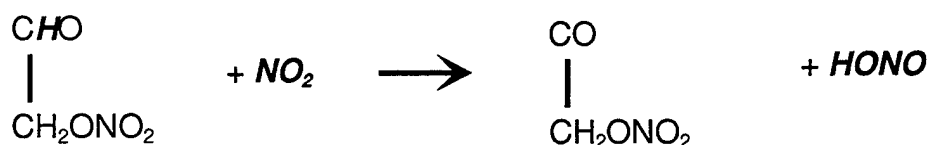
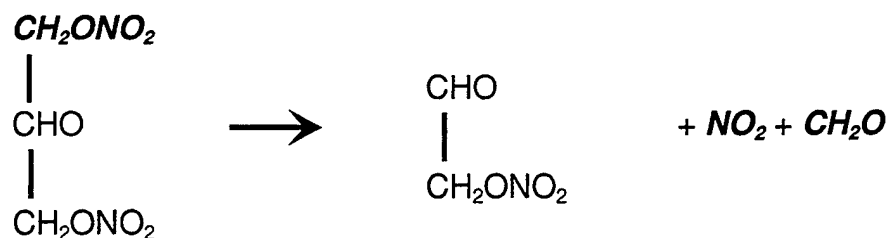
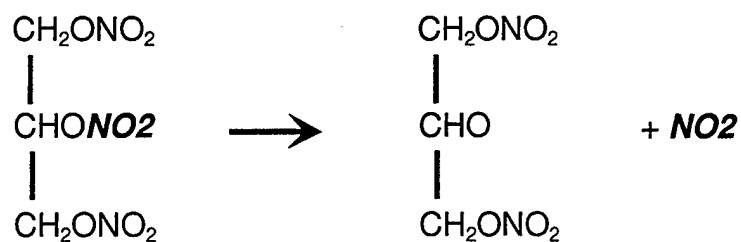


Figure 2. Levy's Rationalization for NG Decomposition Scheme.

Table 1. Hypothetical Condensed-Phase Decomposition Pathways for NG

Name	Overall Reaction
Levy [11]	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow 2 \text{NO}_2 + \text{HONO} + 2 \text{CH}_2\text{O} + \text{CO}$
Hatch [1]	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow 3 \text{NO}_2 + 2 \text{CH}_2\text{O} + \text{HCO}$
MSM1	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow 2 \text{NO}_2 + \text{HONO} + \text{CH}_2\text{O} + 2 \text{HCO}$
MSM2	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow 2 \text{NO}_2 + \text{HONO} + \text{CH}_2\text{O} + \text{H}_2 + 2 \text{CO}$
MSM3	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow \text{NO}_2 + 2 \text{HONO} + 3 \text{HCO}$
MSM4	$\text{NG (C}_3\text{H}_5\text{N}_3\text{O}_9) \rightarrow 3 \text{HONO} + 2 \text{HCO} + \text{CO}$

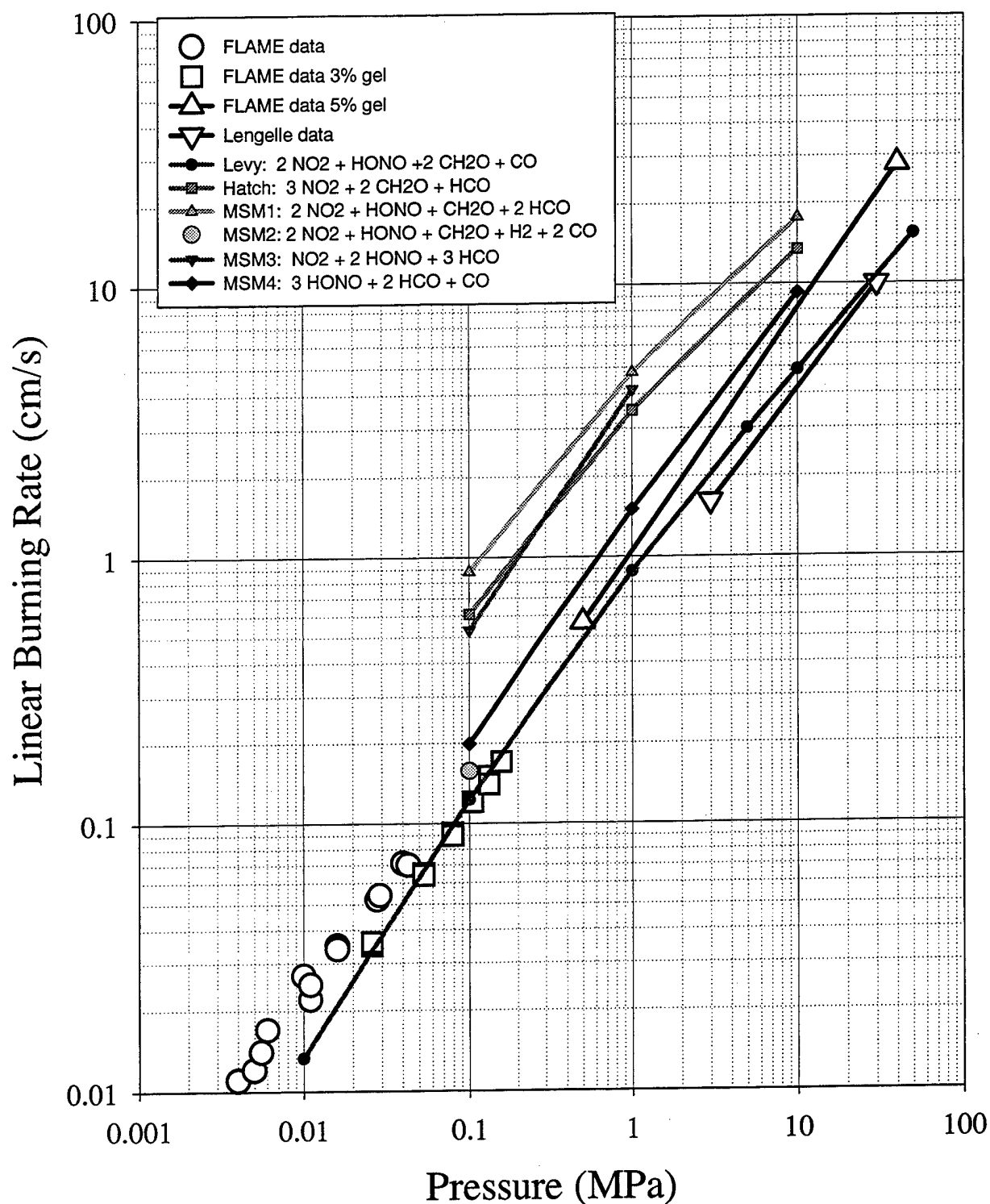


Figure 3. Calculated Burning Rates Based on the Assumption of Alternative Condensed-Phase Decomposition Paths.

agreement with experiment using the more complete mechanism. The interesting thing about the results in Figure 3 is that the burning rate of NG varies about an order of magnitude among the different sets of decomposition products. This implies that enormous control over burning rate might be obtainable if the course of decomposition can be intentionally altered.

An obvious question to ask concerning these results is whether those decomposition sets leading to the faster burning rates do so because of higher implied condensed-phase heat release. Table 2 compares the computed burning rates and heat feedback to the enthalpies of reaction from NG at 298 K to the gas-phase products at the surface temperature. It is clear that there is, in fact, no correlation between this heat of reaction and the burning rate. Moreover, all of the heats of reaction are endothermic. On the other hand, the heat feedback does correlate perfectly with the burning rate, suggesting that the relative gas-phase reactivity of the product molecules outweighs their condensed-phase endothermicity.

Table 2. Heats of Reaction for Condensed-Phase Decomposition Sets

Product Set	Burning Rate (cm/s)	Heat Feedback (kcal/cm ² -s)	C-Phase Heat of Rxn ΔH (cal/g)
Levy [11]	0.89	0.18	21
MSM4	1.51	0.62	12
Hatch [1]	3.50	2.55	30
MSM3	4.14	3.81	40
MSM1	4.80	4.05	35

4. Effects of Chemical Additives

It has always been hoped that theoretical modeling might some day contribute to the problem of the effects of chemical additives on the burning rate of propellants. However, only with the relatively recent advent of chemically specific modeling with elementary reactions was there any real prospect for realizing these hopes. It is the intention of this section to demonstrate that such theoretical guidance to the formulator is becoming feasible.

A systematic approach is needed to compare the effects of one additive to another in a quantitative sense. One propellant-formulation strategy is to add enough additive to bring the mixture to a zero oxygen balance. This approach affords a rational method of determining the amount of each additive appropriate for comparison purposes. The oxygen balance is defined as that amount of oxygen one must add or subtract to have all oxygen appear in either H_2O or CO_2 . NG has a positive oxygen balance of 3.5% (i.e., it has an oxygen surplus). Thus, we compute that one must add one third of a mole of NH_3 to neutralize each mole of NG. For comparison, we examined several other additives. We are, of course, limited here to those fuel molecules that are already in our reaction mechanism.

As a first demonstration of the effects of additives on propellant flames, we took the converged values of burning rate and surface temperature ($T_s = 637.1 \text{ K}$, $\dot{m} = 0.7029 \text{ g/cm}^2\text{-s}$) obtained in a calculation of pure NG at 10 atm using Levy's decomposition-product set and the DB2 reaction mechanism as our starting conditions for a steady premixed flame. A number of candidate additives, including NH_3 , HNCO , H_2 , and CH_2O , were then added to the Levy decomposition set in amounts computed to achieve neutral oxygen balance. The flame structure was then computed for the fixed surface temperature and mass flux just given using the PREMIX [8] code. These results are compared to the pure-NG case and the case of a 5% diluent of N_2 and shown in Figure 4. There, one can see that the secondary gas flame for the pure-NG case stands off from the surface by a little over a centimeter. Such distances are typical of the dark-zone length of double-base propellants, which contain NG as a major ingredient. Note that, when the NH_3 is added, the dark-zone length collapses by about a factor of 2. Also, the heat feedback increases by 12%. Normally, when the heat feedback increases, one can expect the burning rate to increase as well. The effect NH_3 has on the dark-zone length may explain why M30 burns with no apparent dark zone, unlike any other gun propellant. A major ingredient (about 48% by weight) in M30 is nitroguanidine (NQ), which is known [12] to supply copious amounts of NH_3 upon decomposition. The case with 10% N_2 added has the expected diluent effect, lowering the heat feedback by 11% but having relatively little effect on the dark-zone length. Note that the addition of HNCO both decreases the dark-zone length, even more than NH_3 and results in a lower heat feedback than the N_2 diluent, indicating a chemical-inhibition effect on the primary flame while, curiously, speeding up the secondary flame. Like NH_3 , HNCO may also be a

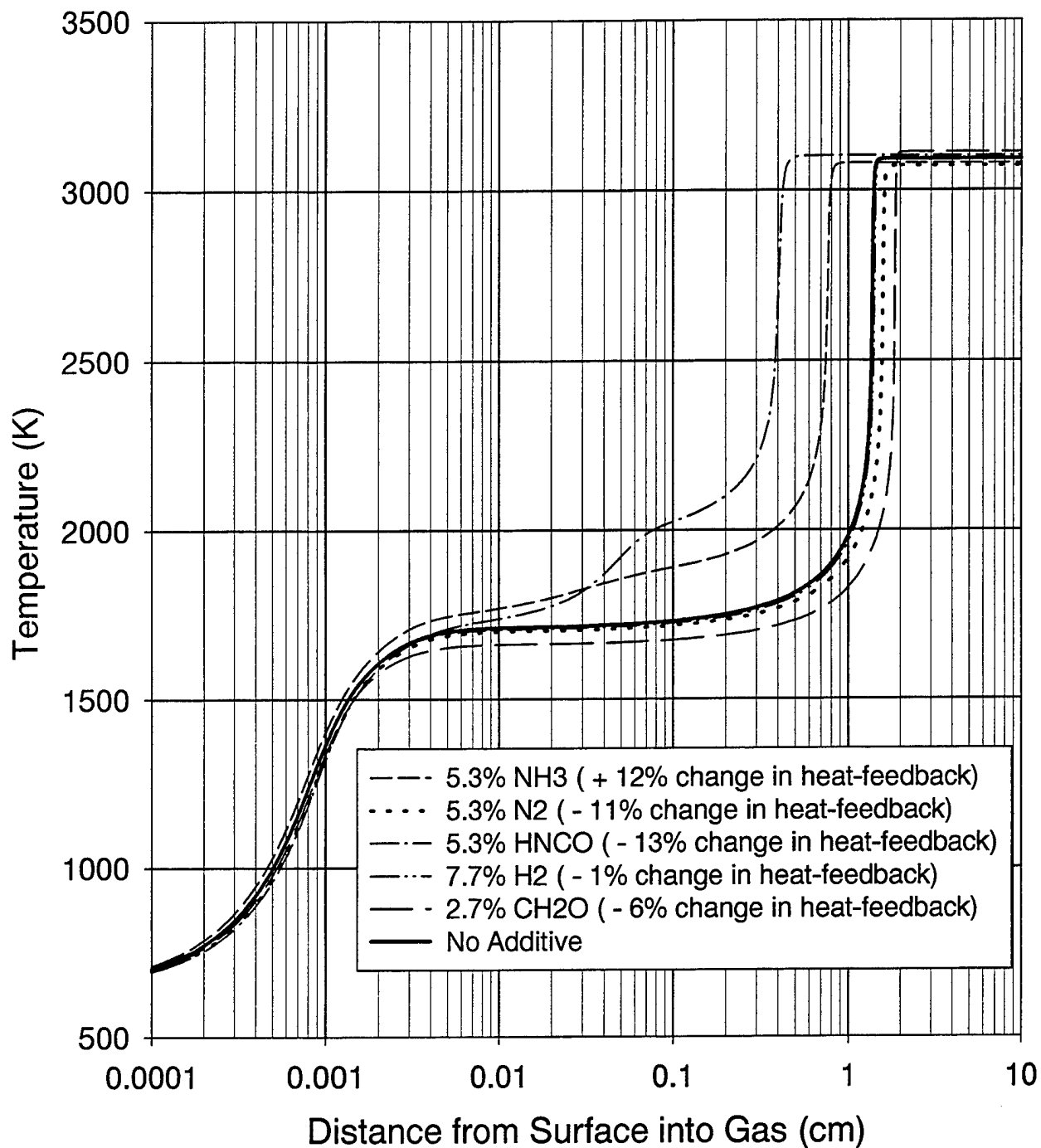


Figure 4. Computed Effect on Heat Feedback of Various Additive Species Combined With Levy Decomposition Products of NG at 10 atm. (Indicated Mole Percentages Produce Zero Oxygen Balance, Except for N₂.)

practical indirect additive since it has been observed [13] to be a major decomposition product of certain AP-propellant ingredients. It should be commented here that decreasing the dark-zone length is thought to be desirable from an interior-ballistic viewpoint, as a shorter dark zone implies faster secondary-flame reactions and, therefore, less ignition delay in a gun. Also note that the addition of sufficient H_2 and CH_2O to lead to a stoichiometric mixture is expected to yield a higher adiabatic flame temperature than the slightly oxygen-rich pure-NG case. One might therefore expect these additives (at the levels used) to yield a significant increase in heat feedback and burning rate. However, these yield much smaller effects than similar additions of NH_3 and $HNCO$ (see legend, Figure 4). CH_2O , in fact, slightly increases the dark-zone length (see Figure 4). The results suggest that near-surface chemical-kinetic effects, which are discussed later, play a role as important as the net overall heat release. Of course, to be certain of the effect of a given additive on the burning rate, the more complex burning-rate problem must be solved. This was done for a few of these additives, as discussed in the next paragraphs.

To compute the quantitative effect of additives on the burning rate, additional assumptions are required, having to do with the effects of condensed-phase mixtures of ingredients. The mass density of the mixture is computed by the method of additive partial molar volumes, that is,

$$\rho_{\text{mix}} = W_{\text{avg}} / \sum_i X_i V_i, \quad (4)$$

where W_{avg} is the average molecular weight, X_i is the mole fraction of ingredient i , and V_i is the molar volume of ingredient i . The mixture mass density is important in calculating the linear burning rate from the mass burning rate. Secondly, we assume that the starting mixture enthalpy is given by the weighted sum of the ingredient enthalpies. This is a reasonable approximation to make, but it ignores any enthalpy of mixing or solution contributions; there is also some ambiguity as to what phase is best to use for the additive enthalpy. Finally, we must, of course, assume that the pyrolysis law is unchanged as a result of these additives. This assumption is reasonable in view of the small amount of each additive.

The results of the burning-rate-with-additive computations are given for the additives NH_3 , CH_2O , and H_2 in Table 3. The enthalpies of all the additives in Table 3 at 298 K are taken as that

Table 3. Effect of Different Chemical Additives on the Burning Rate of NG at 10 atm

Additive	Weight-Percent	Linear Burning Rate (% increase)	Mass Burning Rate (% increase)	Heat Feedback (% increase)
NH ₃	2.4	23	19	25
CH ₂ O	2.2	-2	-4	-5
H ₂	0.44	1	-8	-5

for the gas phase. It should be noted that this assumption could have important consequences for the computed burning rate. For example, if the enthalpy for NH₃ liquid at 298 K is used, the linear burning rate increases by only 12%. This smaller increase reflects the additional energy requirement of the heat of vaporization. Clearly, the calculation of the unreacted-mixture enthalpy is one that may need more sophisticated theoretical guidance. The burning rate with HNCO as additive has not yet been calculated. However, results for the premixed flame structure with this additive, especially the reduction in heat feedback predicted at the surface, suggest that it will reduce burning rate (see legend, Figure 4).

Detailed chemical analysis (i.e., investigation of the chemical rates and kinetic sensitivities for the solutions obtained) was performed on the structure of the flames with NH₃ and HNCO additives in an attempt to understand their predicted strong effects. The analysis yielded likely kinetic explanations for the results. First, it must be noted in all cases that the [H]/[OH] ratio is typically much less than 1.0 near the surface. This result is contrary to the usual situation for near stoichiometric flames where [H] is typically greater than [OH] in the flame zone. [O] is much less than either, as usual for such flames. The small ratio is the result of large quantities of NO₂ near the surface (assumed to be a major component of the intermediate species emanating from the condensed phases for all decomposition pathways used [see Table 1]; the presence of large quantities of NO₂ in the near surface region for nitrate ester and nitramine propellants is undoubtedly correct). The reaction of NO₂ with H atoms,



has one of the largest rate constants known and is the driving force causing the unusually small $[H]/[OH]$ ratio near the surface of even oxygen-lean propellant flames. The ratio typically reverts to $[H]/[OH]$ greater than 1.0 when the NO_2 is consumed. Due to the high reactivity of NO_2 , its consumption is typically complete very close to the surface; in the present examples, this occurs within the first 50 to 100 μm .

In the case of NH_3 , since $[OH]$ is large near the surface, the reaction



dominates conversion to NH_2 . Even near the surface, there is a considerable amount of NO due to reaction [I]. The rate constant for NH_2 to react with NO is also very large, causing the reactions



and



to become important. (In our more recent mechanisms, the products of reaction [IIIa] are changed to $NNH+OH$, which we believe to be the more likely actual products of the reaction. The results are not affected, however, because NNH under these conditions is rapidly, almost completely converted to N_2+H .) Thus, the aforementioned sequence leads to final products and increased heat release due to conversion of some of the NO to N_2 near the surface. Without the additive, little NO is consumed until convection away from the surface at the end of the dark zone. Additionally, reaction [IIIa] is chain branching (i.e., it causes an increase in the growth of reactive radicals, which may play an important role). The increased heat feedback is thus likely the combined result of heat released by NO to N_2 conversion and the larger radical growth rate, both occurring near the surface. Note that, besides increasing heat feedback, NH_3 causes a reduction in the dark zone length (temperature plateau region between about 0.02 and 0.8 cm in

Figure 4, due to slow reaction of NO intermediate). Plots of the NH_3 concentration (not shown) indicate a significant fraction of the NH_3 survives into the dark zone. It seems likely that reactions [II] and [III] initiated by this NH_3 account for the reduction in length of the dark zone, as compared to the pure-NG case, with an additional important contribution from



which matters due to the increased $[\text{H}]/[\text{OH}]$ ratio in the dark zone.

For HNCO as additive, the situation is more complex. Note the curious result, mentioned previously, that the predicted heat feedback is reduced, which one would think indicative of an overall reduced chemical rate near the surface; yet, the predicted dark-zone length is also reduced, which is indicative of a faster overall rate in that region. Near the surface, reaction [I] is very important, similar to all the other neat NG and additive cases. The HNCO thus mainly undergoes reaction with OH,



rather than



which is more usual for stoichiometric flames. There are, however, important secondary contributions from reaction [VI] and from another channel of $\text{OH} + \text{HNCO}$



One would expect the sequence of reaction [Vb] or [VI] followed by reaction [III] to produce an increased heat release, as one might expect for the more usual stoichiometric conditions where $[\text{H}] > [\text{OH}]$. However, here, the heat feedback is predicted to be reduced. This is at least in part due to the fact that the rate of reaction [Va] is faster than reaction [Vb] + reaction [VI], leading to

a higher rate of production of NCO than NH_2 . The reduced heat feedback is thus likely the result of a reduction in radical growth rates due to the radical termination reactions,



and



which the detailed analysis shows are predicted to occur rapidly near the surface; their combined rate is much more rapid than reaction [IIIa]. These reactions convert a highly reactive radical, NCO, to more stable intermediate species or products. Finally, note in Figure 4 that there is a bulge in the temperature profile at about 0.1 cm, indicating that important heat release is occurring there, which likely results in the reduction of dark-zone length. Like the case with NH_3 , it appears the reduction in dark-zone length is due to the survival of a significant fraction of the HNCO additive into the dark-zone plateau region (in this case, between 0.02 and 0.3 cm in Figure 4). In this region, the $[\text{H}]/[\text{OH}]$ ratio becomes larger than 1.0 so that reaction [VI] dominates HNCO consumption. The NH_2 produced undergoes reaction [III] with NO, increasing the global kinetic rate. There may also be a significant contribution increasing the rate by the N_2O produced in reactions [VIIa] and [VIII]. N_2O reacts moderately rapidly at the higher temperatures in the dark zone via



and



Reaction [VIII] increases heat release rate, while reaction [IX] is a chain initiation step (i.e., produces a radical). It seems likely the reaction of the residual HNCO and N_2O leads to the pronounced bulge in the temperature profile for HNCO at about 0.1 cm (see Figure 4). Profiles of HNCO and N_2O (not shown) indicate that both undergo final consumption rapidly at the leading edge of this bulge (about 0.04 cm).

It has long been of interest to find additives that one could use to adjust burning rates of propellants in either direction, hopefully without degradation in other properties. This work has shown that small additions of two simple molecules, NH_3 and HNCO, could increase or decrease, respectively, the burning rate. Also, both species would have the desirable feature of reducing or eliminating the dark zone. It is thought that undesirably long ignition delays in large-caliber guns using nitramine propellants are due to the relatively slow reactions of dark-zone species to produce the energy release associated with the visible flame [14]. Since small amounts of these additives are effective, one might expect that other properties would not be strongly affected. Of course, NH_3 and HNCO are not practical as direct additives. However, there are a number of species that are known to produce these molecules upon pyrolysis and that might be practical; indeed, some of these are now used in propellant formulations (see section 5). Urea, for instance, is known to produce HNCO upon decomposition. We hope to model effects of some of these more complex NH_3 and HNCO precursors in the near future. The semiempirical propellant combustion model developed herein is particularly well suited for such an endeavor because of the availability of the simplifying assumption that NH_3 or HNCO, as well as other species, is produced at the surface. This assumption avoids the difficult issue of kinetics of the complex additives. In the next section, speculations on the effects of one NH_3 precursor as an additive are discussed.

5. Speculations on Practical Burning-Rate Modifiers

The mechanism of the aforementioned NH_3 action invites a further discussion of the M30 case. With NH_3 -modified NG, we found both a collapse of the dark zone and a significant boost in the burning rate. As mentioned previously, NQ, a major ingredient of M30, produces substantial amounts of NH_3 upon decomposition. M30 has no dark zone, consistent with our

NH₃-modified NG case, but it burns no faster than a single-base propellant (M10, 98% NC) and slower than a double-base propellant, a fact that appears to be inconsistent with our model calculation. This apparent inconsistency might be explained as follows. M30 has a nominal composition of 28% NC, 22.5% NG, and 47.7% NQ. It is likely that the large percentage of NQ is responsible for the lack of burning-rate enhancement since it acts to lower the flame temperature of the propellant. Hence, the cooling effect might outweigh the rate-acceleration effect for such major proportions of NQ. We would expect that, if a small amount of NQ (say, 2–5%) were added to either a single- or double-base propellant, the burning rate would be increased and the dark zone diminished. Of course, some of the benefit of the NH₂ from NQ could be diluted by the energy required to break down its parent molecule or to get it into the gas phase, as could be seen in our model calculation's sensitivity to the assumed NH₃ starting enthalpy. Nonetheless, here is a concrete, theoretically inspired idea that could be easily tested. Thus, though the model needs to be further refined and expanded, it can already provide insights of potential worth to the propellant formulator.

6. Conclusions

It has long been a dream that one might use combustion models for guidance in formulating propellants. The calculations presented here indicate that that dream is becoming reality. Though the unrestricted capability of testing any additive is not yet at hand, suggestive guidance on the effects of some additives is now feasible. In addition, we have shown how our ignorance as to the exact chemical course of decomposition in the condensed phase may be used to advantage by calculating the burning-rate dependence on the decomposition path. Those calculations show that one could potentially increase the burning rate of NG by almost an order of magnitude. These studies suggest that the propellant-formulator's art and combustion science are rapidly converging toward a productive synergism.

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Appendix:
Gas-Phase Reaction Mechanism

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Units for the rate parameters are centimeters, seconds, and moles, and, for E, cal/mole. For reactions followed by three numerical parameters, the rate-coefficient expression is $k = AT^b \exp(-E/RT)$. For reactions that appear twice with the phrase "Declared duplicate reaction...", the rate coefficient is computed as the sum of the two three-parameter expressions. For reactions involving a generalized collider species, M, collider efficiencies different than 1.0 are specified. For reactions involving pressure-dependent rate expressions, that is, those with a collider species specified as (+M), three types of expression are used. If "T&H VALUE" occurs in the output, the Tsang and Herron form was used, as described in Tsang and Herron¹ (note that the log expressions used in this source are for base 10)² with constants a_0 and a_1 (if the latter is used) appearing, respectively, on the same line. A version of CHEMKIN modified at the U.S. Army Research Laboratory (ARL) was used to allow this computation. If "TROE centering" occurs, the TROE form was used with appropriate parameters specified on that line. If neither of these is mentioned, the Lindemann form was assumed. Descriptions of the TROE and Lindemann expressions may be found in the CHEMKIN manual.³

¹ Tsang, W., and J. T. Herron. "Chemical Kinetic Data Base for Propellant Combustion. I. Reactions Involving NO, NO₂, HNO, HNO₂, HCN, and N₂O." *Journal of Physical Chemistry*, vol. 20, pp. 609-663, 1991.

² Tsang, W. Private communication. U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1992.

³ Kee, R. J., F. M. Rupley, and J. A. Miller. "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics." SAND89-8009, Sandia National Laboratories, Livermore, CA, September 1989.

				(k = A T**b exp(-E/RT))		
REACTIONS CONSIDERED				A	b	E
1.	NO2(+M)=NO+O(+M)			7.600E+18	-1.27	73290.0
	Low pressure limit:	0.24700E+29	-0.33700E+01	0.74800E+05		
	T&H VALUES	0.95000E+00	-0.10000E-03			
	N2O	Enhanced by	1.500E+00			
	H2O	Enhanced by	4.400E+00			
	N2	Enhanced by	1.000E+00			
	CO2	Enhanced by	2.300E+00			
2.	N2O(+M)=N2+O(+M)			1.260E+12	0.00	62620.0
	Low pressure limit:	0.59700E+15	0.00000E+00	0.56640E+05		
	N2O	Enhanced by	5.000E+00			
	H2O	Enhanced by	7.500E+00			
	N2	Enhanced by	1.000E+00			
	CO2	Enhanced by	3.200E+00			
	O2	Enhanced by	8.200E-01			
3.	H+NO(+M)=HNO(+M)			1.520E+15	-0.41	0.0
	Low pressure limit:	0.89600E+20	-0.13200E+01	0.73500E+03		
	T&H VALUE	0.82000E+00				
	N2O	Enhanced by	5.000E+00			
	H2O	Enhanced by	5.000E+00			
	N2	Enhanced by	1.000E+00			
	CO2	Enhanced by	1.300E+00			
4.	NO+OH(+M)=HONO(+M)			1.988E+12	-0.05	-721.0
	Low pressure limit:	0.50800E+24	-0.25100E+01	-0.67600E+02		
	T&H VALUE	0.62000E+00				
	N2O	Enhanced by	5.000E+00			
	H2O	Enhanced by	8.300E+00			
	N2	Enhanced by	1.000E+00			
	CO2	Enhanced by	1.500E+00			
5.	NO+M=N+O+M			1.400E+15	0.00	148430.0
	N2	Enhanced by	1.000E+00			
	H2	Enhanced by	2.200E+00			
	H2O	Enhanced by	6.700E+00			
	CO2	Enhanced by	3.000E+00			
	N2O	Enhanced by	2.200E+00			
6.	N2+M=N+N+M			3.710E+21	-1.60	225000.0
7.	N2O+N=N2+NO			1.000E+13	0.00	19870.0
8.	NO2+N=N2O+O			5.010E+12	0.00	0.0
9.	NO2+N=NO+NO			3.980E+12	0.00	0.0
10.	NO2+NO2=NO+NO+O2			1.630E+12	0.00	26120.0
11.	NO2+NO2=NO+NO3			9.640E+09	0.73	20920.0
12.	NO2+NO3=NO+NO2+O2			1.400E+11	0.00	3180.0
13.	HNO+NO=N2O+OH			8.510E+12	0.00	29590.0
14.	HNO+O2=HO2+NO			1.000E+13	0.00	25000.0
15.	HNO+NO2=HONO+NO			6.000E+11	0.00	1987.0

16.	HONO+O=OH+NO2		1.200E+13	0.00	5961.0
17.	HONO+OH=H2O+NO2		1.270E+10	1.00	135.0
18.	HNO+O=OH+NO		3.610E+13	0.00	0.0
19.	NH+O=NO+H		5.500E+13	0.00	0.0
20.	NH+O=N+OH		3.720E+13	0.00	0.0
21.	NH+NH=N2+H+H		5.100E+13	0.00	0.0
22.	NH+M=N+H+M		2.650E+14	0.00	75510.0
23.	NH2+NO=N2O+H2		5.000E+13	0.00	24640.0
24.	CH+O2=HCO+O		3.300E+13	0.00	0.0
25.	CH+O=CO+H		5.700E+13	0.00	0.0
26.	CH+OH=HCO+H		3.000E+13	0.00	0.0
27.	CH+CO2=HCO+CO		3.400E+12	0.00	690.0
28.	CH+H=C+H2		1.500E+14	0.00	0.0
29.	C+O2=CO+O		2.000E+13	0.00	0.0
30.	C+OH=CO+H		5.000E+13	0.00	0.0
31.	OH+HCO<=>H2O+CO		5.000E+13	0.00	0.0
32.	HCO+M<=>H+CO+M		1.870E+17	-1.00	17000.0
	H2	Enhanced by	2.000E+00		
	H2O	Enhanced by	1.200E+01		
	CO	Enhanced by	1.500E+00		
	CO2	Enhanced by	2.000E+00		
33.	H+HCO<=>H2+CO		7.340E+13	0.00	0.0
34.	HCO+O=CO+OH		3.000E+13	0.00	0.0
35.	HCO+O=CO2+H		3.000E+13	0.00	0.0
36.	HCO+O2<=>HO2+CO		7.600E+12	0.00	400.0
37.	CO+O(+M)=CO2(+M)		1.800E+10	0.00	2380.0
Low pressure limit: 0.13500E+25 -0.27900E+01 0.41900E+04					
T&H VALUE 0.10000E+01					
	CO	Enhanced by	1.770E+00		
	CO2	Enhanced by	2.700E+00		
	H2O	Enhanced by	5.000E+00		
	N2O	Enhanced by	5.000E+00		
38.	CO+OH=CO2+H		1.510E+07	1.30	-758.0
39.	CO+O2=CO2+O		2.530E+12	0.00	47688.0
40.	HO2+CO=CO2+OH		5.800E+13	0.00	22934.0
41.	H2+O2=2OH		1.700E+13	0.00	47780.0
42.	OH+H2=H2O+H		2.160E+08	1.50	3430.0
43.	O2+H=O+OH		3.520E+16	-0.70	17070.0
44.	O+H2=OH+H		5.060E+04	2.67	6290.0
45.	H+O2+M=HO2+M		3.610E+17	-0.72	0.0
	H2O	Enhanced by	1.860E+01		
	CO2	Enhanced by	4.200E+00		
	H2	Enhanced by	2.900E+00		
	CO	Enhanced by	2.100E+00		
	N2	Enhanced by	1.300E+00		
46.	OH+HO2=H2O+O2		7.500E+12	0.00	0.0

47.	$H+HO_2=2OH$		1.690E+14	0.00	874.0
48.	$O+HO_2=O_2+OH$		1.400E+13	0.00	1073.0
49.	$2OH=O+H_2O$		6.000E+08	1.30	0.0
50.	$2H+M=H_2+M$		1.000E+18	-1.00	0.0
	H2	Enhanced by	0.000E+00		
	H2O	Enhanced by	0.000E+00		
	CO2	Enhanced by	0.000E+00		
51.	$2H+H_2=2H_2$		9.200E+16	-0.60	0.0
52.	$2H+H_2O=H_2+H_2O$		6.000E+19	-1.25	0.0
53.	$2H+CO_2=H_2+CO_2$		5.490E+20	-2.00	0.0
54.	$H+OH+M=H_2O+M$		1.600E+22	-2.00	0.0
	H2O	Enhanced by	5.000E+00		
55.	$H+O+M=OH+M$		6.200E+16	-0.60	0.0
	H2O	Enhanced by	5.000E+00		
56.	$O+O+M=O_2+M$		1.890E+13	0.00	-1788.0
57.	$H+HO_2=H_2+O_2$		6.630E+13	0.00	2126.0
58.	$2HO_2=H_2O_2+O_2$		1.800E+12	0.00	0.0
59.	$H_2O_2+M=2OH+M$		1.300E+17	0.00	45500.0
60.	$H_2O_2+H=HO_2+H_2$		4.820E+13	0.00	7948.0
61.	$H_2O_2+OH=H_2O+HO_2$		1.750E+12	0.00	318.0
62.	$NO+HO_2=NO_2+OH$		2.110E+12	0.00	-479.0
63.	$NO_2+H=NO+OH$		1.300E+14	0.00	361.0
64.	$NO_2+O=NO+O_2$		3.900E+12	0.00	-238.0
65.	$NCO+H=NH+CO$		5.400E+13	0.00	0.0
66.	$NCO+O=NO+CO$		4.520E+13	0.00	0.0
67.	$NCO+N=N_2+CO$		2.000E+13	0.00	0.0
68.	$NCO+OH=NO+CO+H$		2.000E+13	0.00	7500.0
69.	$NCO+M=N+CO+M$		1.140E+23	-1.95	59930.0
	N2O	Enhanced by	5.000E+00		
	H2O	Enhanced by	5.000E+00		
	N2	Enhanced by	1.000E+00		
	CO2	Enhanced by	1.500E+00		
70.	$NCO+NO=N_2O+CO$		8.800E+17	-1.78	790.0
71.	$NCO+NO=CO_2+N_2$		1.130E+18	-1.78	790.0
72.	$NCO+NO_2=CO_2+N_2O$		1.950E+13	-0.26	-620.0
73.	$NCO+NO_2=CO+NO+NO$		1.770E+12	-0.26	-620.0
74.	$NH+O_2=HNO+O$		4.610E+05	2.00	6500.0
75.	$NH+O_2=NO+OH$		1.280E+06	1.50	100.0
76.	$NH+NO=N_2O+H$		3.500E+14	-0.46	16.1
77.	$NH+NO=N_2+OH$		2.160E+13	-0.23	0.0
78.	$N_2O+H=N_2+OH$		2.530E+10	0.00	4550.0
	Declared duplicate reaction...				
79.	$N_2O+H=N_2+OH$		2.230E+14	0.00	16750.0
	Declared duplicate reaction...				
80.	$NNH+O=N_2O+H$		1.400E+14	-0.40	477.0
81.	$NNH+O=NO+NH$		3.300E+14	-0.23	-1013.0

82.	$N_2O+O=N_2+O_2$		1.400E+12	0.00	10800.0
83.	$N_2O+O=NO+NO$		6.920E+13	0.00	26600.0
84.	$H+HNO=NH+OH$		3.000E+14	0.00	18000.0
85.	$NH+OH=N+H_2O$		5.000E+11	0.50	2000.0
86.	$NH+N=N_2+H$		3.000E+13	0.00	0.0
87.	$N+H_2=NH+H$		1.600E+14	0.00	25140.0
88.	$HNO+H=NH_2+O$		3.500E+15	-0.30	28200.0
89.	$NH_2+O=NH+OH$		6.750E+12	0.00	0.0
90.	$NH_2+OH=NH+H_2O$		4.000E+06	2.00	1000.0
91.	$NH_2+H=NH+H_2$		4.000E+13	0.00	3650.0
92.	$NH_2+NH=N_2H_2+H$		1.500E+15	-0.50	0.0
93.	$NH_2+N=N_2+H+H$		7.200E+13	0.00	0.0
94.	$NH_2+O_2=HNO+OH$		4.500E+12	0.00	25000.0
95.	$NH_2+NH_2=N_2H_2+H_2$		5.000E+11	0.00	0.0
96.	$NH_2+NH_2=NH+NH_3$		5.000E+13	0.00	10000.0
97.	$NH_2+NH_2=N_2H_3+H$		1.790E+13	-0.35	11320.0
98.	$NH_2+NH_2+M=N_2H_4+M$		2.980E+47	-9.44	9680.0
99.	$NH_2+NO_2=N_2O+H_2O$		2.840E+18	-2.20	0.0
100.	$NH+NO_2=N_2O+OH$		1.000E+13	0.00	0.0
101.	$N_2H_4+H=N_2H_3+H_2$		1.000E+12	0.50	2000.0
102.	$N_2H_4+OH=N_2H_3+H_2O$		3.000E+10	0.68	1290.0
103.	$N_2H_4+O=N_2H_3+OH$		2.000E+13	0.00	1000.0
104.	$N_2H_3=N_2H_2+H$		1.200E+13	0.00	58000.0
105.	$N_2H_3+H=N_2H_2+H_2$		1.000E+12	0.50	2000.0
106.	$N_2H_3+OH=N_2H_2+H_2O$		3.000E+10	0.68	1290.0
107.	$N_2H_3+O=N_2H_2+OH$		2.000E+13	0.00	1000.0
108.	$N_2H_2+M=NNH+H+M$		5.000E+16	0.00	50000.0
	H2O	Enhanced by	1.500E+01		
	O2	Enhanced by	2.000E+00		
	N2	Enhanced by	2.000E+00		
	H2	Enhanced by	2.000E+00		
109.	$N_2H_2+H=NNH+H_2$		5.000E+13	0.00	1000.0
110.	$N_2H_2+O=NH_2+NO$		1.000E+13	0.00	0.0
111.	$N_2H_2+O=NNH+OH$		2.000E+13	0.00	1000.0
112.	$N_2H_2+OH=NNH+H_2O$		1.000E+13	0.00	1000.0
113.	$N_2H_2+NH=NNH+NH_2$		1.000E+13	0.00	1000.0
114.	$N_2H_2+NH_2=NH_3+NNH$		1.000E+13	0.00	1000.0
115.	$NH_2+NO=N_2+H+OH$		9.300E+11	0.00	0.0
116.	$NH_2+NO=N_2+H_2O$		2.000E+20	-2.60	924.0
117.	$NH_3+OH=NH_2+H_2O$		2.040E+06	2.04	566.0
118.	$NH_3+H=NH_2+H_2$		5.420E+05	2.40	9917.0
119.	$NH_3+O=NH_2+OH$		9.400E+06	1.94	6460.0
120.	$NH_3+M=NH_2+H+M$		2.200E+16	0.00	93470.0
121.	$NNH+NO=N_2+HNO$		2.000E+13	0.00	0.0
122.	$NNH+H=N_2+H_2$		1.000E+14	0.00	0.0
123.	$NNH+OH=N_2+H_2O$		5.000E+13	0.00	0.0

124. $\text{NNH} + \text{NH}_2 = \text{N}_2 + \text{NH}_3$	5.000E+13	0.00	0.0
125. $\text{NNH} + \text{NH} = \text{N}_2 + \text{NH}_2$	5.000E+13	0.00	0.0
126. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$	1.295E+07	1.88	-958.0
127. $\text{H} + \text{HNO} = \text{H}_2 + \text{NO}$	4.460E+11	0.72	655.0
128. $\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$	2.000E+13	0.00	1000.0
129. $\text{N} + \text{NO} = \text{N}_2 + \text{O}$	3.270E+12	0.30	0.0
130. $\text{O} + \text{NO} = \text{N} + \text{O}_2$	3.800E+09	1.00	41375.0
131. $\text{NO} + \text{H} = \text{N} + \text{OH}$	1.700E+14	0.00	48800.0
132. $\text{HNO} + \text{HNO} = \text{N}_2\text{O} + \text{H}_2\text{O}$	3.630E-03	3.98	1190.0
133. $\text{N}_2\text{O} + \text{NO} = \text{N}_2 + \text{NO}_2$	4.290E+13	0.00	47130.0
134. $\text{NO} + \text{NO} + \text{NO} = \text{N}_2\text{O} + \text{NO}_2$	1.070E+10	0.00	26800.0
135. $\text{HOCO} + \text{M} = \text{OH} + \text{CO} + \text{M}$	2.190E+23	-1.89	35270.0
136. $\text{CO} + \text{NO}_2 = \text{NO} + \text{CO}_2$	9.040E+13	0.00	33780.0
137. $\text{CH} + \text{NO}_2 = \text{HCO} + \text{NO}$	1.010E+14	0.00	0.0
138. $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$	3.210E+12	0.00	28810.0
139. $\text{NNH} = \text{N}_2 + \text{H}$	3.000E+08	0.00	0.0
Declared duplicate reaction...			
140. $\text{NNH} + \text{M} = \text{N}_2 + \text{H} + \text{M}$	1.000E+13	0.50	3060.0
Declared duplicate reaction...			
141. $\text{HNO} + \text{NO} + \text{NO} = \text{HNNO} + \text{NO}_2$	1.700E+11	0.00	2100.0
142. $\text{HNNO} + \text{NO} = \text{NNH} + \text{NO}_2$	3.200E+12	0.00	270.0
143. $\text{HNNO} + \text{NO} = \text{N}_2 + \text{HONO}$	2.600E+11	0.00	810.0
144. $\text{HNNO} + \text{M} = \text{H} + \text{N}_2\text{O} + \text{M}$	2.200E+15	0.00	21600.0
145. $\text{HNNO} + \text{M} = \text{N}_2 + \text{OH} + \text{M}$	1.000E+15	0.00	25600.0
146. $\text{HCO} + \text{NO} = \text{HNO} + \text{CO}$	7.230E+12	0.00	0.0
147. $\text{O} + \text{CH}_2\text{O} \rightleftharpoons \text{OH} + \text{HCO}$	3.900E+13	0.00	3540.0
148. $\text{O} + \text{CH}_2\text{OH} \rightleftharpoons \text{OH} + \text{CH}_2\text{O}$	1.000E+13	0.00	0.0
149. $\text{O} + \text{CH}_3\text{O} \rightleftharpoons \text{OH} + \text{CH}_2\text{O}$	1.000E+13	0.00	0.0
150. $\text{O} + \text{CH}_3\text{OH} \rightleftharpoons \text{OH} + \text{CH}_2\text{OH}$	3.880E+05	2.50	3100.0
151. $\text{O} + \text{CH}_3\text{OH} \rightleftharpoons \text{OH} + \text{CH}_3\text{O}$	1.300E+05	2.50	5000.0
152. $\text{O}_2 + \text{CH}_2\text{O} \rightleftharpoons \text{HO}_2 + \text{HCO}$	1.000E+14	0.00	40000.0
153. $\text{H} + \text{HCO} (+\text{M}) \rightleftharpoons \text{CH}_2\text{O} (+\text{M})$	1.090E+12	0.48	-260.0
Low pressure limit: 0.13500E+25 -0.25700E+01 0.14250E+04			
TROE centering: 0.78240E+00 0.27100E+03 0.27550E+04 0.65700E+04			
H2	Enhanced by	2.000E+00	
H2O	Enhanced by	6.000E+00	
CO	Enhanced by	1.500E+00	
CO2	Enhanced by	2.000E+00	
154. $\text{H} + \text{CH}_2\text{O} (+\text{M}) \rightleftharpoons \text{CH}_2\text{OH} (+\text{M})$	5.400E+11	0.45	3600.0
Low pressure limit: 0.12700E+33 -0.48200E+01 0.65300E+04			
TROE centering: 0.71870E+00 0.10300E+03 0.12910E+04 0.41600E+04			
H2	Enhanced by	2.000E+00	
H2O	Enhanced by	6.000E+00	
CO	Enhanced by	1.500E+00	
CO2	Enhanced by	2.000E+00	
155. $\text{H} + \text{CH}_2\text{O} (+\text{M}) \rightleftharpoons \text{CH}_3\text{O} (+\text{M})$	5.400E+11	0.45	2600.0

Low pressure limit: 0.22000E+31 -0.48000E+01 0.55600E+04				
TROE centering: 0.75800E+00 0.94000E+02 0.15550E+04 0.42000E+04				
H2	Enhanced by	2.000E+00		
H2O	Enhanced by	6.000E+00		
CO	Enhanced by	1.500E+00		
CO2	Enhanced by	2.000E+00		
156.	H+CH2O<=>HCO+H2	2.300E+10	1.05	3275.0
157.	H+CH2OH(+M)<=>CH3OH(+M)	1.800E+13	0.00	0.0
Low pressure limit: 0.30000E+32 -0.48000E+01 0.33000E+04				
TROE centering: 0.76790E+00 0.33800E+03 0.18120E+04 0.50810E+04				
H2	Enhanced by	2.000E+00		
H2O	Enhanced by	6.000E+00		
CO	Enhanced by	1.500E+00		
CO2	Enhanced by	2.000E+00		
158.	H+CH2OH<=>H2+CH2O	2.000E+13	0.00	0.0
159.	H+CH3O(+M)<=>CH3OH(+M)	5.000E+13	0.00	0.0
Low pressure limit: 0.86000E+29 -0.40000E+01 0.30250E+04				
TROE centering: 0.89020E+00 0.14400E+03 0.28380E+04 0.45569E+05				
H2	Enhanced by	2.000E+00		
H2O	Enhanced by	6.000E+00		
CO	Enhanced by	1.500E+00		
CO2	Enhanced by	2.000E+00		
160.	H+CH3O<=>H+CH2OH	3.400E+06	1.60	0.0
161.	H+CH3O<=>H2+CH2O	2.000E+13	0.00	0.0
162.	H+CH3OH<=>CH2OH+H2	1.700E+07	2.10	4870.0
163.	H+CH3OH<=>CH3O+H2	4.200E+06	2.10	4870.0
164.	H2+CO(+M)<=>CH2O(+M)	4.300E+07	1.50	79600.0
Low pressure limit: 0.50700E+28 -0.34200E+01 0.84350E+05				
TROE centering: 0.93200E+00 0.19700E+03 0.15400E+04 0.10300E+05				
H2	Enhanced by	2.000E+00		
H2O	Enhanced by	6.000E+00		
CO	Enhanced by	1.500E+00		
CO2	Enhanced by	2.000E+00		
165.	OH+CH2O<=>HCO+H2O	3.430E+09	1.18	-447.0
166.	OH+CH2OH<=>H2O+CH2O	5.000E+12	0.00	0.0
167.	OH+CH3O<=>H2O+CH2O	5.000E+12	0.00	0.0
168.	OH+CH3OH<=>CH2OH+H2O	1.440E+06	2.00	-840.0
169.	OH+CH3OH<=>CH3O+H2O	6.300E+06	2.00	1500.0
170.	HO2+CH2O<=>HCO+H2O2	1.000E+12	0.00	8000.0
171.	CH+H2O<=>H+CH2O	1.713E+13	0.00	-755.0
172.	CH2OH+O2<=>HO2+CH2O	1.800E+13	0.00	900.0
173.	CH3O+O2<=>HO2+CH2O	4.280E-13	7.60	-3530.0
174.	HCO+HNO=CH2O+NO	6.000E+11	0.00	2000.0
175.	CH2O+NO2=HCO+HONO	8.020E+02	2.77	13730.0
176.	HCO+NO2=CO+HONO	1.240E+23	-3.29	2355.0
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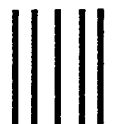
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