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# Nitramine Deflagration: Reduced Chemical Mechanism for Primary Flame Facilitating Simplified Asymptotic Analysis

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**It is proposed that nitramines burn by staged combustion in which most of the energy is released in a secondary flame that is convective-reactive in character and that has a negligible influence on the deflagration velocity. A nearly adiabatic condition is then achieved at the end of the primary gas-phase flame that precedes this secondary flame, the flame temperature $T_f$ at the adiabatic point lying between about 1200–1500 K. The detailed gas-phase chemical kinetics for this primary flame are addressed here. The chemistry is reasoned to involve initially a set of elementary steps that result in HONO, HCN, $H_2CO$, and $N_2O$ as decomposition products obtained in an overall endothermic manner at temperatures in the vicinity of 1000 K, followed by steps that exothermically produce NO, $N_2$, $CO_2$, $H_2O$, and HOCN at a rate found through systematic reduction of the chemistry to be that of bimolecular HONO decomposition. Systematic reduction of the chemistry of the initial process enables the ratio of HCN to $H_2CO$ to be determined as a function of pressure, thereby predicting the pressure dependence of $T_f$ and showing that this primary flame temperature decreases gradually with increasing pressure. Because of the activation energy of HONO decomposition, this decrease causes the effective pressure exponent of the exothermic reduced step to be less than two, and thereby reproduces the experimentally observed pressure exponent of about 0.8 for the deflagration velocity. Excellent agreement is obtained with measured deflagration velocities of cyclotrimethylenetrinitramine.**

## Introduction

Many solid propellants now employ crystalline cyclic nitramines $(H_2CNNO_2)_n$ such as cyclotrimethylenetrinitramine (RDX) ($n$ = 3) and cyclotetramethylenetetranitramine (HMX) ($n$ = 4) as major ingredients.[1] Knowledge of the combustion mechanisms of such propellants would be improved by increased understanding of the deflagration of the pure nitramine crystals. A number of theories for the steady, planar deflagration of these pure nitramines have now been published, as in presentations of our earlier work on the subject.[2,3] During deflagration, some decomposition occurs in a liquid layer on the surface of the crystal, and further decomposition and combustion occur in the gas phase. It has been found[2,3] that measured deflagration velocities are predicted very well if it is assumed that the controlling chemistry in the gas phase can be described by a one-step, exothermic process with a fixed heat release giving a flame temperature around 1350 K and with an empirically determined overall reaction order of 1.6. However, the underlying chemical–kinetic reasons for the resulting agreement between theory and experiment are unknown. The objective of the investigation reported here is to try to explain this success, beginning with a description of the gas-phase chemistry at the level of the elementary steps involved.

The present study is focused mainly on RDX, rather than on HMX, because an appreciable amount of liquid-phase decomposition occurs for HMX as a consequence of the higher boiling point of its liquid. Our previous theoretical analysis[3] predicts that the percentage of the decomposition that occurs in the liquid phase during HMX deflagration at an initial temperature of 293 K varies from about 35% at 1 atm to about 15% at 1000 atm. In addition, bubbling melt layers are observed experimentally on pure HMX surfaces during deflagration,[4] further establishing the importance of the liquid phase. The liquid-phase decomposition complicates the gas-phase analysis by providing to the gas appreciable amounts of decomposition products whose chemical compositions in deflagration really are unknown today (despite very extensive research). If liquid-phase decomposition can be neglected, then only a simple evaporative equilibrium condition for the nitramine itself is needed at the liquid-gas interface (except for addressing two-phase flow effects[3] that are peripheral to the normal burning velocity), and uncertainties in the analysis of the gas-phase chemistry are thereby reduced appreciably. When RDX is selected, its greater volatility enables liquid-phase decomposition to be neglected with excellent accuracy. Our previous work[3] indicates that the percentage of decomposition that occurs in the liquid phase during RDX deflagration is always less than 0.1%. Even in his computational study of RDX deflagration with detailed chemistry (which has numerous uncertainties because of the guesses that had to be made for unknown elementary rate constants), Melius[5] reports that only about 5–7% of the decomposition was found to occur in the condensed phase (and that departures from surface evaporative equilibrium are less than 1%). It is therefore safe to assume that RDX deflagration is dominated by its gas-phase chemistry. The information obtained from studying RDX will be relevant to HMX, for which more than 60% of the decomposition occurs in the gas phase, through mechanisms that certainly parallel those of RDX entirely.

Although gas-phase chemistry in nitramine deflagration was addressed in some of the earlier studies,[2,6,7] only three previous investigations[5,8,9] have attempted to apply known rate constants of elementary steps. The need for more work in this area has been emphasized in a recent survey.[10] All three of the published studies employed numerical integrations of steady-state, one-dimensional conservation equations, and from 77 to 158 different elementary steps were included in the different investigations. Only one[5] took into account steps involving decomposition of the original nitramine vapor molecules; the other two[8,9] began with (different) sets of assumed initial de-

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composition products. This latter approach fails to address fully the gas-phase chemical kinetics of RDX deflagration. In the present study, an appreciable amount of attention is devoted to the initial gaseous nitramine decomposition, and the previously employed mechanisms for this[5] are completely revised.

It is widely maintained that there are two gas-phase stages in nitramine deflagration; intermediate molecules such as NO and HCN are relatively stable and may be considered to burn in a second stage. The experimental evidence for this comes mainly from observations on deflagrations of nitramine powders in various matrices because of experimental complications in working with pure nitramines. Unless confined by a tough epoxy casing[4] (that can interfere with detailed measurements), single crystals crack under thermal stresses during deflagration, giving irregular surfaces and erratic burning rates. In addition, pure pressed powders are prone to having the tiny solid crystals transported convectively off the surface during deflagration, leading to very thick two-phase flame zones and greatly enhanced flame propagation velocities, often termed, convective burning.[4] These problems are aggravated by increasing pressure; the epoxy approach fails at high pressure and convective burning is dominant above a critical pressure.[4] Lower convective velocities at reduced pressures help to eliminate convective burning, and the lower burning rates lengthen distances, facilitating spacial resolution. When advantage was taken of this by burning RDX at 0.5 atm,[11] the first stage was found through a mass-spectrometric study to be so thin that its existence could only be inferred from the measured intermediate reaction products in the gas at the apparent surface of the condensed phase. These observed products, about equal amounts of $H_2O$, NO, and HCN, about one-third as much $N_2$ and $CO_2$, about one-fourth as much CO and $N_2O$, and about one-tenth as much $NO_2$ and HNCO (all on a molar basis), are taken here as fundamental data for helping to define the final conditions of the primary (first-stage) gas-phase flame.

In some[12] (but not all[13]) matrices of the types used in composite propellants, the nitramine forms a fairly homogeneous melt with the binder at the burning surface, and the slow-burning matrix material remains essentially inert in the primary flame, lengthening the dark zone at the beginning of the secondary flame to such an extent that it is readily discernible visually at pressures up to about 20 atm. Niioka and Mitani attempted to take advantage of this by working with pressed pellets of HMX powder in 3 or 6% wax or in 20 or 30% polystyrene (by mass), embedding stretched thermocouple wires in these pellets, and recording temperature profiles during deflagration at pressures up to about 20 atm; some of their results have been reported.[14] The wax is inert enough to react negligibly in the primary flame. Despite the great difficulties in such experiments, they found a clear indication of a temperature plateau in the range of roughly 1200–1500 K in the gas, approximately consistent energetically with the observed[11] intermediate products. Such plateaus have been postulated in previous[1,2,6] theories that propose two-stage gas-phase combustion. In the present work the plateau is presumed to be of sufficient extent that conductive energy feedback from the secondary flame can be neglected. The secondary flame is considered to be convective–reactive, so that the primary flame controls the deflagration velocity, and attention is then focused only on the chemistry in the primary flame. In this respect, the present study has little relationship to two[8,9] of the earlier detailed-kinetic studies.

The previous computational studies[5,8,9] have not revealed the two-stage gas-phase chemistry in deflagration. In particular, the computed temperature profile is smooth, all the way to temperatures above 3000 K, and it does not exhibit a plateau.[5] This must reflect defects in the elementary kinetics and rate parameters for the primary flame. An objective of the present investigation is to help to identify and correct these defects. In the presentation of one earlier study[8] it is stated that the transport effects were neglected in the first approximation; this is reasonable in that the study appears to address only the secondary flame, which is nearly convective–reactive. It is of interest that the two-stage behavior was seen in ignition computations in which transport effects were absent[5] and some primary-stage chemistry was included. This finding suggests that many of the essential elements required to describe the primary flame already are available. It remains only to determine how these elements need to be augmented to obtain suitable primary-flame descriptions for the deflagration.

## Decomposition

Rough values of energies of the covalent bonds found in RDX and HMX are[15] 50 kcal/mol for the N–N bond, 60 kcal/mol for the C–N bond, and 90 kcal/mol for the C–H bond. As described in thorough reviews,[16] because of these bond-energy estimates, in the absence of definitive experimental data, it has generally been assumed that the initial step in the decomposition mainly involved breaking of the N–N bond, the weakest in the molecule. In condensed-phase decomposition, this cleavage does indeed initiate the fastest paths, as demonstrated in significant recent clarifications of condensed-phase decomposition mechanisms.[17–23] However, for the gas-phase decomposition that is of interest here, the much higher temperatures will alter the mechanism substantially. The highest temperature achieved in a gas-phase decomposition study is on the order of 1000 K (comparable with temperatures in the primary flame), accomplished by stimulating vibrational excitations through use of IR multiphoton absorption in a molecular beam of RDX molecules crossed by a light beam from a pulsed $CO_2$ laser.[24] Estimated reaction times in that experiment also are comparable with those estimated in the primary flame, on the order of 10 $\mu$s. This work, which involved only unimolecular decomposition because of the low pressure, indicated that the dominant primary decomposition channel under those conditions is concerted symmetric triple fission to produce three $H_2CNNO_2$ fragments, which subsequently undergo secondary dissociation to yield HCN, HONO, $H_2CO$, and $N_2O$. Extensive use of these results will be made here because the conditions achieved appear to have come closer than those of any other fundamental kinetic studies to the conditions existing in the primary gas-phase flame, not in pressure, of course, but temperature (or energy level) is more crucial and the heating rates and maximum temperatures of the other studies are too low.

Notationally, let RDXN, RDXN1, and RDXN2, respectively, denote cyclic compounds $(H_2CNNO_2)_2(H_2CN)$, $(H_2CNNO_2)\cdot(HCN)(H_2CN)$, and $(H_2CNNO_2)(H_2CN)_2$. Through mass spectrometry[24] two primary dissociations were identified as

$$\mathrm{RDX} \rightarrow 3\mathrm{H_2CNNO_2} \tag{R1}$$

$$\mathrm{RDX} \rightarrow \mathrm{RDXN} + \mathrm{NO_2} \tag{R2}$$

and four secondary dissociations were observed to be

$$\mathrm{RDXN} \rightarrow \mathrm{RDXN1} + \mathrm{HONO} \tag{R3}$$

$$\mathrm{RDXN} \rightarrow \mathrm{RDXN2} + \mathrm{NO_2} \tag{R4}$$

$$\mathrm{H_2CNNO_2} \rightarrow \mathrm{HCN} + \mathrm{HONO} \tag{R5}$$

$$\mathrm{H_2CNNO_2} \rightarrow \mathrm{H_2CO} + \mathrm{N_2O} \tag{R6}$$

Among these steps only (R5) and (R6) are exothermic, the latter being much more so. Branching ratios for all six steps were determined[24]; e.g., reaction (R1) was found to be twice as fast as (R2), indicating predominance of the concerted symmetric fission over the N–N bond breaking. In addition, the rate of (R3) was found to be nearly 10 times that of (R4), and the rate of (R5) more than five times that of (R6). Of the products appearing here, RDXN1 and RDXN2 are the least stable, and since the neighboring C–N bond is significantly weakened, it can easily rupture, opening the ring. It is assumed here that a sequence of C–N cleavages rapidly ensues, resulting in

$$\mathrm{RDXN1} \rightarrow \mathrm{H_2CNNO_2 + H_2CN + HCN} \qquad \mathrm{(R7)}$$

$$\mathrm{RDXN2} \rightarrow \mathrm{H_2CNNO_2 + 2H_2CN} \qquad \mathrm{(R8)}$$

The eight steps identified previously result in a set of three- and four-atom decomposition products to which available elementary reaction-rate descriptions[5,10,25] can be applied. There is, however, a significant difficulty with this result. Since all of the steps are unimolecular, the predicted distribution of decomposition products is independent pressure, and that prevents agreement from being obtained with the observed pressure dependence of the deflagration velocity. For example, if these unimolecular steps are presumed to control the rate, then the pressure exponent is found to be 0.5, whereas if bimolecular reactions among the decomposition products are controlling, then the exponent is 1.0, and there is no compromise that results in the constant exponent of about 0.8 over the more than three orders of magnitude of pressure, from less than 1 atm to more than 1000 atm, seen experimentally.[4] To circumvent this problem, it is necessary to introduce a bimolecular step in the initial decomposition. Moreover, it is desirable that this step involve only those molecules appearing earlier, rather than radicals from the primary flame, for example, because it is necessary to keep the initial decomposition separated from the reaction zone of the primary flame if the pressure exponent is to remain constant. That is, the decomposition is occurring around 1000 K, while the temperature of the primary reaction zone will exceed 1200 K, in the present description.

Among the molecules appearing previously, $NO_2$ is the most powerful chain initiator and a sufficient amount of $NO_2$ should be available from reaction (R2). It is reasonable to presume that $NO_2$ can abstract an H atom from RDX, according to

$$\mathrm{RDX + NO_2 \rightarrow RDXH + HONO} \qquad \mathrm{(R9)}$$

where RDXH denotes $(H_2CNNO_2)_2(HCNNO_2)$. With RDXH1 and RDXH2 used as shorthand for $(H_2CNNO_2)(HCN)(HCNNO_2)$ and $(H_2CNNO_2)(H_2CN)(HCNNO_2)$, respectively, by analogy with the observed decomposition of RDXN, we propose that

$$\mathrm{RDXH \rightarrow RDXH1 + HONO} \qquad \mathrm{(R10)}$$

$$\mathrm{RDXH \rightarrow RDXH2 + NO_2} \qquad \mathrm{(R11)}$$

with the same branching ratios as reactions (R3) and (R4) [although this branching ratio, as well as that of (R3) and (R4), is inconsequential in the present work]. It would be of interest to try to test these assumptions by crossing RDX and $NO_2$ beams in mass-spectrometric experiments. Just as with steps (R7) and (R8), ring-opening followed by further C–N scissions is taken here to lead to

$$\mathrm{RDXH1 \rightarrow H_2CNNO_2 + HCNNO_2 + HCN} \qquad \mathrm{(R12)}$$

$$\mathrm{RDXH2 \rightarrow H_2CNNO_2 + HCNNO_2 + H_2CN} \qquad \mathrm{(R13)}$$

The decomposition of $HCNNO_2$ may proceed bimolecularly according to

$$\mathrm{HCNNO_2} + M \rightarrow \mathrm{HCN + NO_2} + M \qquad \mathrm{(R14)}$$

Finally, with the availability of $NO_2$, the $H_2CN$ produced here in (R13), as well as that from steps (R7) and (R8), is likely to be especially vulnerable and to disappear through the H abstraction

$$\mathrm{H_2CN + NO_2 \rightarrow HCN + HONO} \qquad \mathrm{(R15)}$$

which can remove $H_2CN$ and all remaining $NO_2$ from the system.

If reactions (R5) and (R6) are momentarily ignored on the basis that they may be the slowest of the preceding steps in the decomposition zone, then a 13-step decomposition mechanism is obtained, the overall effect of which is the endothermic process

$$\mathrm{RDX} \rightarrow 2\alpha\mathrm{HCN} + 2\alpha\mathrm{HONO} + (3 - 2\alpha)\mathrm{H_2CNNO_2} \qquad \mathrm{(A)}$$

where $\alpha$ is the fraction of the RDX disappearances that does not involve step (R1). Stated differently, in this scheme RDX goes away only by reactions (R1), (R2), and (R9), and while (R1) produces three monomer units, (R2) and (R9) eventually produce only one, through (R7), (R8), (R12), and (R13), with the remaining species eventually arriving at HCN + HONO through the other steps. If $x$ denotes the distance normal to the surface of the deflagrating solid, with $x = 0$ at the liquid-gas interface, and if $\omega_i$ denotes the molar reaction rate per unit volume for step (R1), then

$$\alpha = \frac{\int_0^\infty (\omega_2 + \omega_9)\,\mathrm{d}x}{\int_0^\infty (\omega_1 + \omega_2 + \omega_9)\,\mathrm{d}x} \qquad (1)$$

Reinstating now reactions (R5) and (R6) to obtain the full 15-step decomposition, we obtain from reaction (A) the overall decomposition process

$$\mathrm{RDX} \rightarrow A(\mathrm{HCN + HONO}) + B(\mathrm{H_2CO + N_2O}) \qquad \mathrm{(I)}$$

where

$$A = 3 - \beta(3 - 2\alpha), \qquad B = \beta(3 - 2\alpha) \qquad (2)$$

in which the fraction of the $H_2CNNO_2$ that decays by step (R6) is

$$\beta = \frac{\int_0^\infty \omega_6\,\mathrm{d}x}{\int_0^\infty (\omega_5 + \omega_6)\,\mathrm{d}x} \qquad (3)$$

The overall decomposition reaction (I) indicates a breakdown of RDX to (HCN + HONO) and ($H_2CO + N_2O$), the ratio of the concentrations of these two sets of decomposition products being $A/B$, which is dependent on the fractions $\alpha$ and $\beta$. The ratio $A/B$ is significant because the subsequent chemistry in the exothermic reaction zone of the primary flame proceeds to different products for these two sets of reactants, resulting energetically in a flame temperature that depends on $A/B$. This flame temperature influences the deflagration rate and a variation of it with pressure will contribute to the pressure exponent of the burning velocity. Since steps (R5) and

(R6) are both unimolecular, the fraction $\beta$ is independent of pressure (the same conclusion would follow if both were bimolecular). However, since reaction (R9) is bimolecular, Eq. (1) with the unimolecular steps (R1) and (R2) shows that $\alpha$ increases with pressure. Since (R1) is faster than (R2) or (R9), this increase is small. If (R9) were neglected, then the observed[24] branching ratio would correspond to $\alpha = 1/3$; including (R9) would increase $\alpha$ above this low-pressure limiting value by an amount that increases with the pressure $p$. The increase is sufficiently gradual that the weak power-law fit

$$\alpha = 0.32p^{0.068} \tag{4}$$

can be justified, with $p$ in atm, giving $\alpha = 0.32$ at 1 atm and $\alpha = 0.52$ at 1000 atm, a change of less than a factor of 2. This result was motivated by kinetic computations, adjusted slightly to improve the burning-velocity agreement; further study of the decomposition region is desirable to test it more thoroughly. Although the molecular-beam experiments[24] have $0.12 \leq \beta \leq 0.35$, with $\beta \approx 0.2$ representing the most likely value, in the present work it was found necessary to select the upper limit for burning-velocity agreement, and the value

$$\beta = 0.35 \tag{5}$$

was employed. Of all the reactions introduced here so far, only (R2) and (R15) appear in the analysis of Melius,[5] and so the results must be expected to be quite different.

The gaseous decomposition reaction (I) is slightly exothermic for the choices of parameters given here; it is endothermic or nearly energetically neutral and cannot be very exothermic for any choices that do not involve unreasonably small ratios $A/B$. It is assumed that this chemistry goes to completion prior to the more strongly exothermic primary reaction zone. With this assumption, Eqs. (2), (4), and (5) provide all of the information about the decomposition that is needed for analyzing the primary heat-release zone and obtaining the burning velocity. It would, however, be worthwhile to proceed with a more thorough analysis of the structure of the decomposition region. The first question to address is whether this region is broad or narrow compared with the total thickness of the primary flame. Because of the dominance of reaction (R1) and its likely high activation energy probably exceeding 30 kcal/mol, it seems most reasonable to treat the decomposition region as being narrow, to assign it a reactive– diffusive character, and to apply to it activation–energy asymptotics based on the activation energy of (R1). All three initiation steps in the chemistry are endothermic and can be treated similarly. For example, the H–ONO bond strength is about 18 kcal/mol less than the C–H bond strength, so that (R9) is endothermic and probably has an activation barrier not much in excess of the endothermicity, giving it an activation energy between about 10–25 kcal/mol. Steady-state approximations may be introduced for the intermediates in this reaction zone, including $NO_2$, and an outer structure will be obtained in which RDX diffuses in from upstream while the products of step (I) diffuse out, both upstream and downstream, their convection balancing their diffusion to give zero flux in the upstream region. The resulting equations would provide not only the concentration profiles of the species within this reaction zone, but also its location, determined by both the prefactor and the activation energy of the specific reaction-rate constant of (R1). Such an analysis is not pursued here because of uncertainties in rate parameters and because it is unnecessary for obtaining predictions of burning velocities.

## Heat-Release Zone

The least stable of the four products of the overall decomposition step (I) is HONO, which dissociates according to

$$HONO + M \rightarrow OH + NO + M \tag{R16}$$

when the temperature becomes high enough. The stability of the NO released in this process is relatively high, comparable with that of HCN, so that $A$ moles of NO and HCN are produced in the primary flame for each mole of RDX consumed, and these will all burn in the secondary flame (except for a small amount of HCN, to be discussed later in this article). Since formaldehyde is the species most vulnerable to hydroxyl, reaction (R16) can be followed by

$$H_2CO + OH \rightarrow HCO + H_2O \tag{R17}$$

$$HCO + OH \rightarrow CO + H_2O \tag{R18}$$

the formyl intermediate readily producing carbon monoxide, so that the overall effect is

$$2OH + H_2CO \rightarrow CO + 2H_2O \tag{B}$$

as could be expressed formally by introducing a steady-state approximation for HCO. Although the resulting CO is oxidized to $CO_2$ by OH, this process progresses more slowly. Introduction of a steady-state approximation for $H_2CO$ as well would result in the overall step

$$HONO + \tfrac{1}{2}H_2CO \rightarrow NO + \tfrac{1}{2}CO + H_2O \tag{C}$$

at the rate of reaction (R16).

The CO oxidation proceeds by

$$CO + OH \rightarrow CO_2 + H \tag{R19}$$

which releases a hydrogen atom that can produce $N_2$ by

$$N_2O + H \rightarrow N_2 + OH \tag{R20}$$

Although the activation energy of reaction (R20) prevents it from being important at low temperatures, in the latter part of the flame where (R19) is proceeding [since its specific reacting-rate constant is appreciably less than those of (R17) and (R18)], the temperature can be high enough for (R20) to be considered to proceed right after (R19); in other words, a steady-state approximation for H can be introduced, giving the overall process

$$CO + N_2O \rightarrow CO_2 + N_2 \tag{D}$$

at the rate of (R19). If step (D) is considered to be fast enough for a CO steady state to apply, then the overall process of (C) becomes

$$HONO + \tfrac{1}{2}H_2CO + \tfrac{1}{2}N_2O \rightarrow NO + \tfrac{1}{2}CO_2 + \tfrac{1}{2}N_2 + H_2O \tag{E}$$

at the rate of (R16).

With the values obtained for $A$ and $B$ in the decomposition (I), there is more than enough HONO to consume all of the $H_2CO$ and $N_2O$ by step (E). Since (R16) continues to produce NO and OH after this, the question arises as to the fate of the excess OH in the primary flame. After it builds up to sufficient concentrations, the step 2 $OH \rightarrow H_2O + O$ may be anticipated, but there is no conveniently rapid outlet for the O atom, except possibly routes that lead to its appearing ultimately as $O_2$, which is not observed. It is proposed here that the steps

$$OH + HCN \rightarrow HOCN + H \tag{R21}$$

$$OH + HCN \rightarrow HNCO + H \tag{R22}$$

and possibly also

$$OH + HCN \rightarrow HCNO + H \tag{R23}$$

although slower than (R19), in total are rapid enough to prevent the 2OH step from becoming important by effectively consuming the relatively small amount of OH that remains. The H atoms produced in this process can further remove OH, for example, by

$$H + OH + M \rightarrow H_2O + M \qquad (R24)$$

This OH depletion then terminates the primary flame by eliminating all active radicals. The effect of the three HCN steps is approximated as (R21) at an enhanced rate, since literature values give its rate to be faster than the other two at the conditions of the primary-flame heat-release zone, and since its intermediate heat of formation affords a reasonable compromise in energetic calculations. This particular selection is not critical, and slightly better values of $\beta$ would be obtained from the deflagration fit if (R22) had been used instead. However, conformation considerations favor (R21), and even though the more stable form HNCO is observed experimentally, it could be expected to be formed later, for example, on the boundary between the primary flame and the dark zone, or even possibly in the sampling apparatus. The important thing is to get the OH out, so that there will be a dark zone. The addition of (R21) and (R24) to (E) results in

$$\begin{aligned} &A(HONO) + B(H_2CO + N_2O) + (\tfrac{1}{2}A - B)(HCN) \rightarrow A(NO) \\ &\quad + B(CO_2 + N_2) + (\tfrac{1}{2}A - B)(HOCN) + (\tfrac{1}{2}A + B)(H_2O) \end{aligned} \qquad (F)$$

as the overall result of (R16). The total effect of the primary-flame heat-release process may thus be written as

$$\begin{aligned} &A(HCN + HONO) + B(H_2CO + N_2O) \rightarrow A(NO) \\ &\quad + B(CO_2 + N_2) + (\tfrac{1}{2}A + B)(H_2O + HCN) \\ &\quad + (\tfrac{1}{2}A - B)(HOCN) \end{aligned} \qquad (II)$$

the rate of which will then be $A$ times the rate of the elementary reaction (R16). There are various sources of elementary rate data[5,25–28] for a few of the 24 individual steps involved in the resulting two-step overall mechanism.

The assumption that the overall heat-release process (II) is controlled by the rate of (R16) rests on the hypothesis that reactions (R17–R24) are sufficiently rapid in the primary-flame exothermic zone. This hypothesis is favored by the observation that the activation energies of all of these steps are small compared with that of (R16). The 40 kcal/mol activation energy of (R16) strongly favors application of activation-energy asymptotics (AEA) to this step. The detailed structure of the exothermic zone in the vicinity of its hot boundary could be quite complex, with step (D) then (R21) and (R24) occurring after the other steps, but these nevertheless are presumed to be reactive–diffusive rather than reactive–convective (or reactive–convective–diffusive), so that AEA for (R16) at the flame temperature associated with (II) determines the burning velocity. In a more detailed analysis, it might be found that the endothermicity of (R21–R23) leads to a temperature overshoot in the exothermic zone, locally enhancing the rates of these steps and of (R20), but such effects are not considered here because their influences are likely to be comparable with the inaccuracy associated with the downstream adiabaticity condition.

There are a number of additional uncertainties involved in this description. For example, there is some indication[24] that the decomposition step (R6) may result in appreciable amounts of $HNO_2$ rather than only HONO, and $HNO_2$ decomposition would give HNO + O and H + $NO_2$, consistent with the reported[11] small amounts of $NO_2$ in the products, not present in step (II). If appreciable amounts of $HNO_2$ are present, then the exothermic chemistry needs to be revised, a task not addressed here because of uncertainty about formation of this less stable species. Also, the measurements[11] are reported to show small amounts of HNCO rather than the HOCN appearing in step (II). However, there are likely to be uncertainties in the results of the measurements, and on the basis of the information currently available, step (II) as derived here seems to be the most reasonable selection. Further experimental investigations to test the present hypothesis might either support the present procedures or demonstrate that revisions are required.

According to step (II), the total heat release per unit mass of reactant (calorie/gram) in the exothermic zone is found from Eq. (2) to be

$$q_{II} = 83 + 463\beta(3 - 2\alpha) \qquad (6)$$

The total heat released in the gas per unit mass of gaseous RDX is

$$q_g = 100 + 562\beta(3 - 2\alpha) \qquad (7)$$

and the final temperature of the primary flame is[3]

$$T_f = T_u + (q_g - q_v)/c_p \qquad (8)$$

where $T_u$ is the initial temperature of the solid RDX, $c_p = 0.35$ cal/g K is the average specific heat at constant pressure for the gas, and $q_v$ is the energy required to vaporize the solid (140 cal/g for RDX). Substitution of Eqs. (4) and (5) into Eqs. (7) and (8) gives

$$T_f = T_u + 1573(1 - 0.23p^{0.068}) \qquad (9)$$

all pressures being in atmosphere and temperatures in Kelvin. Between 1–1000 atm for $T_u = 300$ K, Eq. (9) can be fit with less than 2% error by the formula

$$T_f = 1512p^{-0.0225} \qquad (10)$$

The resulting mild decrease in $T_f$ with increasing $p$ is a consequence of the increase in $\alpha$, i.e., the increase in the rate of (R9), which leads to a reduction in the amount of $H_2CNNO_2$ produced in step (A) and a corresponding reduction in $B$ and increase in $A$ in step (I), i.e., a decrease in the amount of $H_2CO$ + $N_2O$ produced, so that the products of step (II) have less of the most stable species $CO_2$ (especially), $H_2O$ and $N_2$. It is mostly the formaldehyde oxidation that releases the heat, and the formaldehyde comes only from $H_2CNNO_2$ in reaction (R6), so that the $H_2CNNO_2$ reduction with increasing $p$ through the competition of (R9) reduces $T_f$. Because of measurement difficulties, this reduction has not been verified experimentally.[14] The decrease is small; e.g., $T_f$ is calculated to decrease from 1512 to 1294 K when $p$ increases from 1 to 1000 atm.

There is no need to present the details of the application of AEA to the calculation of the burning velocity because, once step (II) is identified as the heat-release process that occurs at the rate of the bimolecular reaction (R16), the analysis becomes exactly equivalent to previously presented theory,[29] it being necessary only to pay careful attention to energetics for matching to the convective–diffusive upstream zone downstream from the location at which step (I) occurs. The Zel'dovich number (often denoted by $\beta$)[29] for this problem is $Ze = (q_{II}E_{II})/(R^0 c_p T_f^2)$, where $E_{II} = 39.2$ kcal/mol denotes the activation energy of (R16), and $Ze$ takes on values between 10–20, which are large enough that only the leading term in the asymptotic expansion needs to be retained. In terms of the HONO mole fraction $X_{HONO}$, the rate of step (II) is

$$\omega_{II} = A[p/(R^0T)]^2 X_{HONO} A_{II} \exp[-E_{II}/(R^0T)] \qquad (11)$$

where $A_{II} = 1.9 \times 10^{16}$ cm$^3$/mol-s is the prefactor of the specific reaction-rate constant for (R16). These rate parameters are fits to data from the literature.[30] Since the only reactant in Eq. (11), HONO, appears unimolecularly, the burning-velocity formula is that[29] for a unimolecular process. Thus, the burning velocity is

$$r = \frac{1}{\rho_p}\left[\left(\frac{2\lambda}{c_p}\right)\left(\frac{c_p T_f}{q_{II}}\right)^2\left(\frac{R^0 T_f}{E_{II}}\right)^2 A^2 \bar{W}\left(\frac{p}{R^0 T_f}\right)^2 A_{II} \exp\left(-\frac{E_{II}}{R^0 T_f}\right)\right]^{1/2} \tag{12}$$

where $\rho_p$ denotes the solid density, $\lambda$ the thermal conductivity, and $\bar{W}$ the average molecular weight. Taking $\rho_p = 1.8$ g cm$^3$ for RDX, $\lambda/c_p = 5 \times 10^{-4}$ g/cm-s, and $\bar{W} = 34.2$ g/mol for the final products, by use of Eqs. (9) or (10) as well as Eq. (6) and previously given values for parameters and expressions for $A$, we obtain from Eq. (12) an explicit expression for $r$ as a function of $p$. The main influence of $p$ in this expression occurs through the $p^2$ factor and through the variation of $T_f$ with $p$ in the exponential term. For RDX at $T_u = 300$ K, the result can be fit within 5% accuracy to the power-law expression

$$r = 0.032 p^{0.85} \text{ cm/s} \tag{13}$$

Similar power-law fits can readily be obtained for other values of $T_u$.

## Discussion of Results

Figure 1 is a schematic diagram of the deflagration model developed here. After melting, decomposition in the liquid layer occurs to an important extent for HMX, but to a negligible extent for RDX; the influence of the two-phase flow in the structure of this layer has been described previously[3] and therefore is not shown in Fig. 1. Under all conditions, most of the reactant enters the gas phase through equilibrium vaporization and it is the chemical fate of this gaseous nitramine that has been addressed in the present study. Somewhere in the gaseous preheat zone the endothermic decomposition step (I) occurs, as illustrated, and it goes to completion, leaving another convective–diffusive zone upstream from the primary-flame reactive–diffusive zone in which the exothermic step (II) occurs. This zone, the primary-flame heat-release zone of the previous section, is denoted for brevity as the gaseous primary reaction zone in Fig. 1. The deflagration rate is controlled by the chemical reaction rate, Eq. (11), in this zone, since near-adiabaticity conditions prevail at its downstream boundary. The secondary flame, in which most of the heat release and the main temperature rise occur, proceeds in a convective–reactive manner on a longer length scale than that of the processes analyzed here, longer than the primary-flame standoff distance,[31]

$$x_f = \frac{\lambda}{r \rho_p c_p} \ln\left[\frac{q_g}{c_p(T_s - T_u) + q_v}\right] \tag{14}$$

where $T_s$ is the surface temperature and the condensed-phase specific heat has been approximated as $c_p$ of the gas. Equation (14) gives $x_f \leq 200\mu$ for all $p \geq 1$ atm and a substantial decrease in $x_f$ with increasing $p$, so that experimental resolution of the structures of the layers studied here would be exceedingly difficult.

Figure 2 shows the predicted liquid-surface and primary-flame temperatures, as well as $x_f$, as functions of $p$ for RDX with an initial temperature of 300 K. The mild decrease in $T_f$ and the somewhat stronger increase in $T_s$ with increasing $p$ are evident here. These results are generally consistent with experimentally measured temperatures, to the extent that these difficult measurements can be completed. The manner in which $T_s$ is calculated has been presented in detail previously,[2,3] and therefore, is not repeated here.

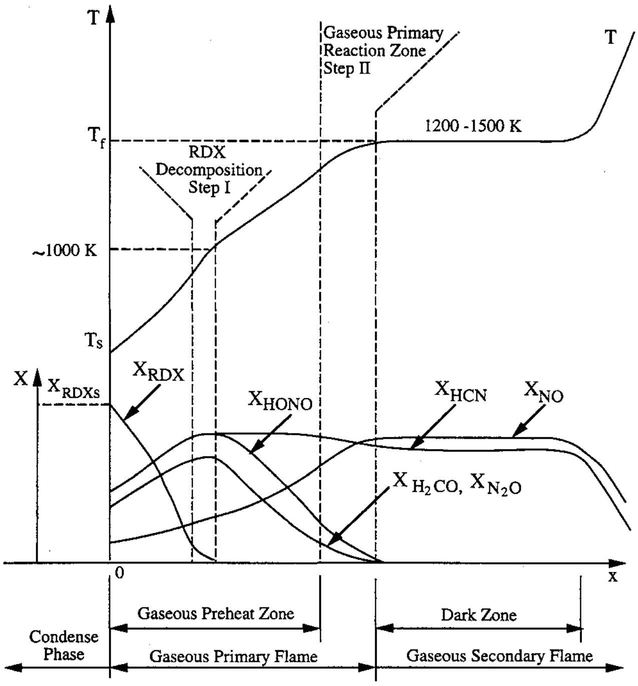

**Fig. 1 Schematic diagram of the deflagration model, showing temperature $T$ and mole-fraction $X_i$ profiles with distance $x$.**

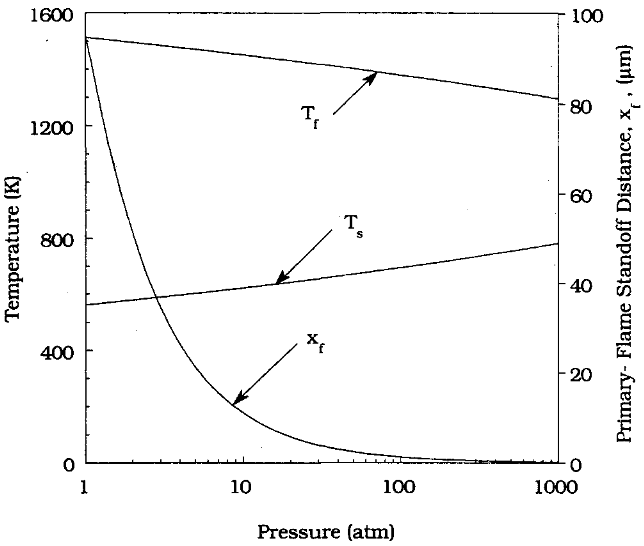

**Fig. 2 Pressure dependence of the primary-flame and liquid-surface temperatures and of the primary-flame standoff distance, for RDX at an initial temperature of 300 K.**

Figure 3 exhibits deflagration velocities as functions of pressure for RDX at $T_u = 300$ K. The excellent agreement with experiment[32,33] is clearly evident here. Thus, the theory is quite successful in predicting measured burning velocities, even with the approximate values that have been employed for various parameters and that should be made more accurate in the future.

Despite this success it is important to question whether the model is correct. It has been seen that many idealizations are involved and that many uncertainties remain to be tested in future studies. The branching ratio for reactions (R1) and (R2) is a crucial element, and it is questionable that the ratio in themolecular-beam experiment applies in the deflagration, al-

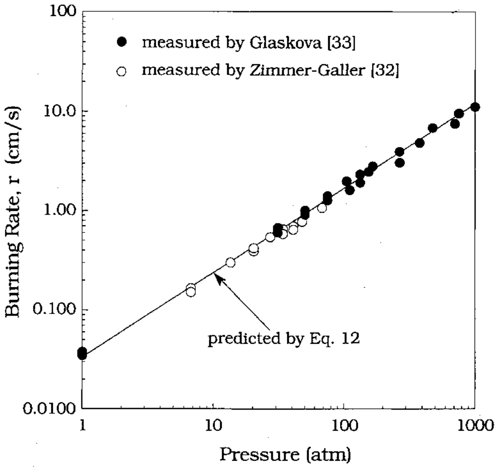

**Fig. 3 Pressure dependence of the deflagration velocity of RDX at an initial temperature of 300 K, according to experiment[31,32] (points) and to the present theory (curve).**

though there could well be a constant pressure-independent high-temperature limit for this ratio that was revealed in the molecular-beam study. For the branching ratio of reactions (R5) and (R6), to avoid having an unreasonably small amount of heat release in the primary flame, we need more formaldehyde than found in the molecular beam, and we are forced to presume that all of the $H_2CNNO_2$ left over in the beam gives formaldehyde in the deflagration. For example, we may possibly assume that $H_2CNNO_2$ survives in the flame to a higher temperature than achieved in the molecular beam, giving it a greater propensity for the route (R6). A number of other chemical–kinetic simplifications have been detailed earlier.

Especially noteworthy is the result that excellent burning-rate agreement can be achieved by assuming that the rate of the bimolecular HONO decomposition reaction (R16) controls the burning velocity. First of all, it is essential that this step remain bimolecular and it is relevant to ask whether that is consistent with known falloff behavior. Although there are uncertainties in falloff as well, published[5] falloff parameters for this step give a pressure of about 200 atm in the middle of the falloff range. Such a value is high enough that it is safe to assume bimolecularity without greatly affecting calculated burning velocities up to 1000 atm, but at least above that pressure a decrease in the burning-rate exponent should be anticipated if additional physical effects do not intervene. Better falloff information for the HONO decomposition is needed. Secondly, it is an oversimplification to place the entire direct deflagration-velocity burden on this single reaction and such an assumption can best be viewed as an initial approximation useful for increasing understanding of the deflagration mechanism.

From this viewpoint, it seems better to ask how inaccurate the model is, rather than whether it is correct. The model has provided a potentially useful simplified picture of the deflagration chemistry that controls the burning velocity. It then becomes possible to begin with the model and to introduce into it corrections for phenomena that it does not include. A general method for introducing corrections for additional elementary chemical steps that have been ignored is given in an earlier study[34] of a related flame. Corrections also should be considered for possible continuation of the decomposition step (I) into the reaction zone of the exothermic step (II) and for energy input from the secondary flame (relaxing adiabaticity). A very relevant and now readily accomplished investigation would be to make purely numerical computations of the flame structure and burning velocity with the chemistry proposed here; such computations could not only show how inaccurate the present ideas are, but could also easily enable additional chemistry to be added gradually, including secondary-flame chemistry, to see what influences the additional steps may have and to ascertain whether their inclusion degrades the burning-velocity agreement to such an extent that revisions in estimated values of some elementary rate constants are needed. We have initiated such an investigation and find that by introducing appropriate elementary steps involving HNCO, to remove radicals such as OH, we can recover a dark zone, which otherwise is not found with the full chemistry, even augmented by the additional steps introduced previously. More work along these lines definitely is needed.

The basic idea of the present model is that with a two-stage gas-phase flame description in which the primary stage controls the burning velocity, the chemical composition achieved at the end of the primary flame depends on the chemical kinetics in that flame and can strongly affect the calculated burning velocity by modifying the flame temperature. With a high overall activation energy, a small change in the flame temperature of the primary flame can have a large effect on the burning velocity, so that relatively small adjustments in primary-flame decomposition chemistry have noticeable influences on burning velocities. It is usual to think of changes in burning velocities as controlled by changes in chemical kinetics. The new element here is to also think of the changes produced by flame-temperature changes that also can be controlled by changes introduced in chemical kinetics. To fit a pressure exponent of about 0.8, unimolecular Arrhenius flame chemistry of appreciable activation energy can be coupled with a flame temperature that increases with increasing pressure, or corresponding bimolecular chemistry can be coupled with a flame temperature that decreases with increasing pressure. The latter has been found here to be more consistent with the known aspects of nitramine deflagration chemistry. It would be very difficult to find an equally simple alternative that can lead to a constant pressure exponent over so wide a range of pressure.

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