

# Multiphase Chemistry Considerations at the Surface of Burning Nitramine Monopropellants

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The surface reaction zone of a solid propellant is increasingly acknowledged as imparting major, if not dominant, characteristics to combustion. An overview of this evolving issue is given. Chemistry considerations associated with the multiphase surface layer of the nitramine monopropellants HMX and RDX are discussed critically. These include global rates, specific decomposition and exothermic reactions, evaporation, and surface temperatures. A chemistry description is offered that involves the competition of two decomposition branches and one strongly exothermic reaction. Based simply on rationally derived reaction rates, reasonable deductions may be made about the surface temperature and reaction-zone thickness during combustion of HMX and RDX.

## I. Introduction

CONCERNS about cost, safety, performance, and ecology have stimulated a march to develop new, high-energy, clean-burning solid rocket propellants. Important departures from past practices are likely to define these efforts. In particular, expanded computational models that predict the combustion behavior may reduce the need for live testing on an exhaustive matrix of ingredients. Acceptance of these combustion models rests on their ability to imitate the observed performance. A great deal of work remains before such reliability is realized. Research that has brought us to the present understanding of conventional solid propellants is a useful guide for future strategies.

An impressive array of chemical and physical details about the gas-phase domain of combustion has been developed and refined by the research community.<sup>1</sup> Recently, the two-phase surface reaction zone of a solid propellant has been physically modeled in considerable detail.<sup>2,3</sup> These important advancements remain limited to some extent by uncertainties about the pathways and rates of specific controlling chemical reactions, especially in the condensed phase and where non-steady combustion is concerned. The fact is that it is enormously difficult to make the necessary experimental measurements on the very thin surface reaction zone, even assuming a one-dimensional combustion wave and a homogeneous monopropellant. However, some of the chemical processes in the surface zone can be outlined by experimental simulation experiments.<sup>4–6</sup>

The opinions and descriptions in this article center on the chemistry and the important role of the surface reaction zone of the nitramine monopropellants RDX and HMX, although

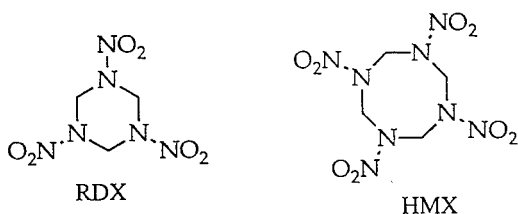
## II. What is the Surface Reaction Zone?

The concept of a surface zone in which chemical reactions take place during combustion is an old one. For example, it was conceptualized in 1950 in publications on double-base propellants.<sup>7–9</sup> Pictorializing the surface zone presents a few problems, some real and some semantic. Alexander et al.<sup>1</sup> illustrate the complexity of the problem by using a figure attributed to Kuo. The real problems mostly arise when defining and solving the equations that properly describe dynamic, interfacial, microscopic, physical, and chemical processes. In this regard Li et al.<sup>2</sup> and Huang et al.<sup>3</sup> analyzed the two-phase zone with considerable care. A simpler and more conventional approach is to define the surface reaction zone as an infinitely thin (superficial) boundary layer from which evaporation and/or decomposition products magically appear.

From the point of view of chemistry, the surface of a burning solid propellant consists of a thin layer in which much of the formulated materials pyrolyze to fuel and oxidizer molecules, which then engage in secondary exothermic reactions. The thickness of this surface reaction zone depends on the temperature, pressure, and formulated ingredients. For example, the surface of HMX and RDX is liquid during combustion at pressures below 67 atm.<sup>10,11</sup> The surface of ammonium perchlorate (AP) is liquid below 50 atm.<sup>12</sup> The liquid layer becomes thinner with increasing pressure because the thermal (or combustion) wave produced by surface multiphase reactions and near-field gas-phase reactions becomes extremely steep.<sup>13</sup> The shape of the one-dimensional combustion wave is defined by the thermophysical properties coupled with the mass, momentum, energy, and species conservation equations.<sup>14</sup> In a simpler approach, Zenin<sup>15</sup> has proposed several generalized equations to govern the surface temperature and heat release in the condensed phase of double-base propellants.

While physics can describe the shape of the combustion wave, the surface reaction zone is a complex, finite, physicochemical entity. Even though the temperature gradient is large at the propellant surface and becomes larger with increasing pressure, the thermal wave still penetrates many unit-cell distances into the repeating lattice of the crystalline monopropellant. For example, a surface reaction zone thickness of 1  $\mu\text{m}$  corresponds to roughly 100 unit-cell lengths of the crystal of HMX or RDX. Hence, the disappearance of an obvious liquid layer at high pressure does not necessarily signal the end of condensed-phase chemistry at the surface.

The surface reaction layer does not refer solely to solid- or liquid-phase pyrolysis reactions of the formulated propellant components. Neither does it refer solely to homogeneous gas-



other materials are mentioned for perspective. The analysis applies primarily to combustion of the homogeneous monopropellant component of the solid rocket propellant.

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phase reactions next to the surface. A more general and accurate description is that of a heterogeneous (or two-phase) zone that includes developing voids and/or bubbles with nanoscopic and microscopic dimensions.<sup>2,3</sup> On the vapor-phase side, the surface boundary is physically rough and dynamically changing owing to the microscopic gasification dynamics. Nominally gas-phase reactions can occur within the multiphase zone and in the near field of the disintegrating surface. Therefore, the operative thickness of the surface reaction zone from the point of view of chemistry is somewhat larger than simply the thickness of the melt layer. However, at least for AP, Hermance<sup>16</sup> had to assume a surface area that is much larger than observed<sup>12</sup> to achieve satisfactory agreement with the characteristics of combustion. Although this detail of Hermance's model seems unreasonable, the ill-defined heterogeneous depiction of the surface is chemically attractive. It enables changes in temperature and pressure to define the changes in species concentrations that are associated with the surface layer. For RDX, Li et al.<sup>2</sup> found that the two-phase surface model and infinitely thin surface model gave similar results in their description of combustion. The distinction between these two models depended largely on the volatility of propellant components.

Finally, the term "melting" is loosely used to describe the formation of the liquid layer on the surface of burning RDX and HMX. However, melting is better reserved for the equilibrium first-order phase transition between the solid and liquid states. To a lesser degree in the case of RDX and a greater degree in the case of HMX,<sup>17</sup> decomposition occurs simultaneously with the change of state. The terms "progressive melting" or simply "liquefaction" more soundly describe this event.<sup>17-20</sup>

### III. Evolving View of the Importance of the Surface Reaction Zone

Of course, models of the combustion of solid propellants contain assumptions based on necessity and wisdom at the time. Evolution of conventional wisdom occurs because of subsequent experimental data and the increase in computational power. Throughout this article, limitations of assumptions are occasionally noted. This is done in the spirit of stimulating thought rather than criticism.

Rather than review combustion models, which has been done expertly elsewhere,<sup>21-27</sup> the focus of this section is to mention whether and how the surface reaction zone has been incorporated. Historically, extensive research and modeling of solid-rocket-propellant combustion was developed in the context of the contribution of the gas phase. In the views of Lewis and von Elbe<sup>28</sup> and Zeldovich,<sup>29</sup> the combustion mechanism was dominated by the gas phase. Belyaev<sup>30</sup> experimentally observed that evaporation followed by gas-phase reaction occurred during combustion of an explosive. Heat from the gas phase was believed to sustain pyrolysis of the surface. This viewpoint, in which gas-phase control was widely accepted, profoundly influenced many subsequent approaches to modeling of steady combustion. It is certainly fair to say that combustion characteristics of highly volatile energetic materials will be overwhelmingly dominated by gas-phase chemistry. However, a wealth of experimental and computational evidence has appeared since these early reports, which reveals that the 1–50- $\mu\text{m}$ -thick surface reaction zone and the ill-defined phase transition to the very near-field gaseous state are major factors or even dominate in determining the combustion characteristics of most solid propellants and their energetic components.

A brief description of several efforts to model the combustion of homogeneous and heterogeneous propellants places the present state of understanding of the surface zone into context. Among the pioneering descriptions of the near field during combustion of solid propellants were the works of Rice and Ginnell,<sup>7</sup> Parr and Crawford,<sup>8</sup> and Wilfong et al.,<sup>9</sup> the

latter of whom developed their ideas in 1941.<sup>22</sup> A sequence of primary and secondary reactions of homogeneous double-base propellants was proposed to account for the surface gasification and the dark zone of the flame against the surface. Heterogeneous propellants were tackled in the granular diffusion flame (GDF) model of Summerfield and co-workers.<sup>31,32</sup> Experimental observations and theoretical work revealed a nonturbulent gaseous zone of up to 1 mm thickness against the surface of an AP composite propellant, and that most of the heat is released within about 100  $\mu\text{m}$  of the surface. Heterogeneity of the surface and the release of heat at the surface were introduced by Hermance<sup>16</sup> in a refinement of the GDF model. This model can certainly be cited as one that sets the stage for incorporation of a finite surface reaction layer into combustion modeling. Subsequent models of Beckstead et al.<sup>12,33,34</sup> and Guirao and Williams<sup>35</sup> both concluded that 70–75% of the heat of AP is released in the condensed-phase surface zone. However, the absence of experimental details about chemistry prompted emphasis to be placed on the transport and spatial aspects of combustion as opposed to the chemical reaction sequences. In fact, the surface zone was set aside in many subsequent descriptions of solid propellant combustion in favor of attention to flame structure. For example, the model of Beckstead et al.,<sup>12,33,34</sup> (BDP) generalized an approach for modeling flame structure and emphasized the major role played by the surface temperature. The petite ensemble model of Glick<sup>36</sup> statistically refined the flame structure according to the effect of different particle sizes of the oxidizer in a composite propellant. The effects of particle size on the combustion characteristics were also refined.<sup>37</sup> Miller attempted to formulate a general model of homogeneous propellant combustion based on a single-step process in each phase.<sup>38</sup>

More recently, models of solid propellant combustion have incorporated multistep kinetics and heat release. The majority of these models retain the simplicity of an infinitely thin surface zone that is merely a source of reactants for the gaseous flame zone. Examples of this approach are summarized first. While such models might be considered to originate from the early descriptions of double-base propellants,<sup>7-9</sup> the model of Guirao and Williams<sup>35</sup> describing the combustion of AP also stands out as a pioneering effort. They incorporate a global decomposition rate for the condensed phase, but specific gas-phase reactions. Subsequent models of AP combustion<sup>39,40</sup> make use of more complex gas-phase reaction schemes, some of which are controversial.<sup>41</sup> An attempt to refine several aspects of the surface zone chemistry of AP has been made.<sup>42</sup> Models of the combustion of HMX and RDX with specific reaction kinetics have been presented.<sup>24,43-52</sup> Widely differing numbers of reactions and species are included in these models, however, many aspects of the gas-phase chemistry have been experimentally verified. In particular, mass spectrometry, in which a quartz microprobe is inserted into the flame to sample the species, is especially useful.<sup>53-55</sup>

The expanding effort to model physicochemical details of the surface reaction layer foretells how its role has become recognized. Reactions involving this heterophase layer are now considered by many workers to play a significant role in controlling the burning rate. The weight of experimental evidence for this belief is growing. Many studies indicate that most of the heat comes from exothermic processes in a thin surface layer and not from the far-field gas phase.<sup>12,15,33-35,56,57</sup> Relevant, but perhaps less convincing, studies are of burn-rate enhancement, which suggest that most of the action occurs in the condensed phase.<sup>58,59</sup>

Although early work on double-base propellants did stress the importance of the surface reaction zone,<sup>7-9</sup> detailed descriptions of the process came later in the articles by Merzhanov<sup>60</sup> and Strunin and Manelis<sup>61</sup> on AP. Combustion models<sup>2,12,33-35,62-64</sup> on nitramines incorporate a finite surface layer in which a global rate of decomposition is assumed. Huang

et al.<sup>3</sup> have used specific reactions in the surface layer as discussed in Sec. V. A major fraction of the heat is released in the surface layer in most models developed by Williams and coworkers<sup>2,35,62</sup> and by Beckstead and coworkers.<sup>12,33-45</sup> Cohen et al.<sup>47</sup> updated the gas-phase kinetics in the model of Ben-Reuven et al.,<sup>63,64</sup> and concluded that most of the heat is released by HMX within 10  $\mu\text{m}$  of the surface. This distance is within the control volume that defines the multiphase zone of a burning surface. Along the same lines Zenin<sup>15</sup> found that 80–90% of the heat is released in the condensed phase during combustion of nitrocellulose. In none of these models or experiments is there an implication that the gas phase can be ignored. The main point is that both the condensed phase and the gas phase must be modeled to achieve truly accurate predictions.

The partitioning of the heat between the condensed phase and gas phase depends on pressure and the formulation of the propellant. In modeling efforts, the relative contributions of each phase depend on the assumptions and parameters chosen. In this article, the focus is on the role played by the rates of several specific chemical reactions in the surface zone of a solid propellant under conditions representative of combustion. This component is but one of the important aspects of the total description of combustion of the solid propellant.

#### IV. Surface Reaction Zone: Description with Global Rates

Global Arrhenius parameters for the surface reaction zone are best viewed as giving only the temperature dependence of the overall process. This definition is broader than process control by the chemical kinetics alone.<sup>65</sup> Equation (1) is the well-known Arrhenius equation for describing the temperature dependence of the rate of conversion,  $d\alpha/dt$ . With the foregoing precautionary comment in mind, the terms

$$\frac{d\alpha}{dt} = (1 - \alpha)^n A e^{-E_a/RT} \quad (1)$$

activation energy  $E_a$ , prefactor  $A$ , and order of the process  $n$  will be retained.

Two types of global Arrhenius parameters for surface processes must be distinguished. These are the surface activation energy and the chemical activation energy. The surface activation energy  $E_s$  is obtained from the pyrolysis law (2). Measured linear regression rates  $\dot{r}$  at various surface temperatures  $T_s$  define the value of  $E_s$ . Surface regression to which Eq. (2) applies is a zero-order process because fresh

$$\dot{r} = A_s e^{-E_s/RT_s} = aP^b \quad (2)$$

reactant replaces gasified products at a constant rate.

Diffusion, vaporization, and reaction rates all contribute to the value of  $E_s$ . In fact, Eq. (2) applies over only limited pressure ranges where the pressure exponent  $b$  remains constant. Nevertheless, surface activation energies have occasionally been mentioned in the same context as chemical activation energies,<sup>66,67</sup> such as bond-breaking steps or bimolecular reactions. It is risky to equate  $E_s$  and  $E_a$ . First, the rate law for the rate-controlling chemical reactions, such as homolyses of specific bonds in the surface reaction zone, is likely to be predominately first-order, which makes the Arrhenius parameters for regression and bond homolysis not directly comparable. Second, the contributions of transport and chemical rates are mixed in  $E_s$ . Third, starting with Merzhanov and Dubovitskii,<sup>68</sup> a number of authors<sup>13,69</sup> have shown that the square of the linear regression rate is related to the Arrhenius parameters of bulk-phase chemical decomposition. Equation (3) shows this relationship for many propellants, where  $T_0$  is the initial temperature,  $d$  is the thermal diffusivity,  $Q$  is the

heat released in the surface layer  $T_s^2$  and  $C_p$  is the heat capacity.

$$\dot{r}^2 = \frac{dT_s^2 A e^{-E_a/RT_s}}{E_a(T_s - T_0 - Q/2C_p)} \quad (3)$$

According to Eq. (3),  $E_s \propto E_a/2$ . In practice, the values of  $E_s$  are indeed usually small<sup>70</sup> compared to the strength of the weakest bond in energetic molecules and the global Arrhenius parameters for decomposition of HMX and RDX<sup>71</sup> that are derived from differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and manometry. Equation (3) has a better chance to predict burn rates than Eq. (2) when the gas and condensed phases are coupled. Other aspects of Eq. (2) are mentioned by Zanotti et al.<sup>72</sup>

The global rates referred to in the title of this section are of the second kind, namely decomposition rates extracted from Eq. (1) by measuring the rate of heat release, pressure increase, or weight decrease. A compilation of published Arrhenius parameters ( $E_a$ ,  $A$ ) for slow thermal decomposition of HMX and RDX in the solid, liquid, and vapor phases reveals poor agreement, irrespective of the phase.<sup>71</sup> For HMX,  $22E_a$  values for the solid phase cover 13–67 kcal/mol. Six values for the liquid phase are  $E_a = 47$ –65 kcal/mol, and six values for the vapor phase are  $E_a = 32$ –53 kcal/mol. For all but one case, the differences among  $E_a$  values are compensated by differences in  $A$ , so that the plot of  $E_a$  vs  $\ln A$  produces an approximately straight line.<sup>71</sup> As a result, the rates of decomposition are roughly the same over the temperature range of measurement. In effect, all of the  $E_a$ - $\ln A$  combinations on this regression line legitimately describe the rate of decomposition. The wide range of  $E_a$  values is caused by differences in the sample characteristics and the experimental conditions. However, extrapolation of the rates from these  $E_a$ - $\ln A$  pairs to another temperature range, such as the one that exists during combustion, gives wildly different predictions.

Several models of combustion of HMX and RDX make use of global rates of decomposition in the liquid and/or gas phases.<sup>2,38,45,47,50,62-64</sup> The values usually chosen lie in the experimentally determined range for slow decomposition, but Mitani and Williams<sup>62</sup> expressed concern about the fact that the Arrhenius parameters required for their model are at the low end of this experimental range. Because of the compensation effect, their choice of values is not cause for concern. Any  $E_a$ - $\ln A$  pair lying on the compensation line, whether measured or not, is a legitimate representation of the rate at some particular set of conditions.<sup>71</sup> There is no single intrinsically "correct" global rate of decomposition of bulk phase HMX or RDX because the determined values depend on the sample characteristics and working conditions.<sup>71</sup> Therefore, in combustion models containing these global rates, the  $E_a$ - $\ln A$  pair should be viewed as an adjustable parameter along the compensation line, as opposed to a parameter that is fixed by the "correct" rate of decomposition. No one can take issue with the  $E_a$ - $\ln A$  combination as long as it resides along the compensation line.

#### V. Surface Reaction Zone: Description with Specific Reactions

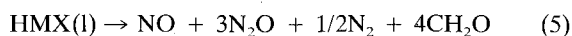
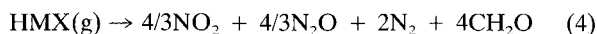
Rather than using phase-dependent global rates of thermal decomposition, many authors of combustion models have employed the rates of specific reactions of the parent molecule and its products. This approach is ultimately preferable to using only phase-dependent global rates because it enables more accurate refinements to be made on the effects of temperature and pressure. Several aspects of this approach are heuristic, which stimulates suspicions and contrary opinions. For example, a critical evaluation<sup>41</sup> of previous gas-phase reaction schemes for combustion of AP<sup>35,39,40</sup> revealed unreasonable assumptions in each case and motivated development

of yet another scheme.<sup>41</sup> Similar uncertainty exists with RDX and HMX, and will no doubt arise in efforts to describe combustion of the next generation of energetic materials.

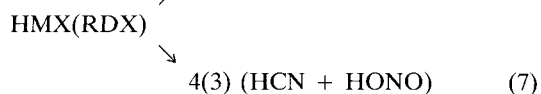
#### A. Thermolysis Reactions of HMX and RDX

The thermal decomposition pathways of RDX and HMX in the condensed phase have become much better defined in recent years.<sup>73</sup> Significant differences exist between reactions that occur at lower temperature/heating rate conditions<sup>74–78</sup> and those at higher temperature/heating rates.<sup>4–6,79,80</sup>

Many combustion models now incorporate the kinetics of specific reactions beginning with decomposition of HMX or RDX. Essentially two schemes have been used. Scheme I [Eqs. (4) and (5)] was the first:



The exothermic reaction (4) in Scheme I appears to have been adopted from the decomposition data of Suryanarayana and Graybush<sup>81</sup> and Cosgrove and Owen,<sup>82,83</sup> which were obtained in the lower temperature/heating rate regime. Reaction (4) has been employed in many combustion models, such as those of Ben Reuven et al., for RDX<sup>63</sup> and HMX<sup>64</sup>; Ermolin et al.,<sup>49</sup> for RDX; Mitani and Williams<sup>62</sup> and Kubota and Sakamoto<sup>84</sup> for HMX. Ben-Reuven et al., use reaction (5) in Scheme I as well for the liquid phase. Scheme I is difficult to accept for the combustion regime because it fails to account for the high level of HCN and the low level of N<sub>2</sub> at the burning surface of RDX found by quartz microprobe mass spectrometry<sup>53–55</sup>:



Scheme II [Eqs. (6) and (7)] is another decomposition pathway that states that rapid thermolysis of HMX and RDX occurs by two competing branches represented by (6) and (7). The formalism for reaction (7) varies, i.e., the products might also be written as H<sub>2</sub>CN + NO<sub>2</sub> or H· + NO<sub>2</sub> + HCN. When written as shown, reaction (6) is exothermic (–29 kcal/mol), whereas (7) is endothermic (+28 kcal/mol) by about the same energy.<sup>51</sup> Scheme II is more attractive than Scheme I because it has experimental support in the gaseous products that are liberated during combustion<sup>53–55</sup> and from a film of HMX or RDX when heated at a high rate to temperatures in the range of the burning surface.<sup>5,80,85</sup> This latter experiment is described later in this article. Scheme II has been adopted in several models of nitramine combustion, many of which predated experimental verification. For example, Price et al.<sup>43</sup> incorporated a portion of Scheme II into the BDP description of nitramine flame structure. However, their proposed temperature dependence of several products of reactions (6) and (7) was opposite that determined subsequently by experiment.<sup>5</sup> More recent models and descriptions<sup>3,46,50,51,86,87</sup> employ (6) and (7), and where used, (6) and (7) appear to be given the correct temperature dependence.

Scheme II cannot be verified directly with a burning solid propellant because the surface reaction zone is spatially very thin and positionally transient, possesses a steep temperature gradient, and has a mixture of phases. Although optical spectroscopy of the gaseous phase close to the surface has been achieved,<sup>88–90</sup> the critical near field at  $\leq 20 \mu\text{m}$  from the surface has not been probed. Therefore, laboratory simulation experiments have been invented<sup>80,91,92</sup> to try to outline the major chemical processes. A reasonably well-controlled technique is T-jump/FTS-IR spectroscopy, in which a “snapshot”

experimental simulation of the surface reaction layer is attempted.<sup>91</sup> This technique has been discussed and modeled sufficiently,<sup>91,93</sup> and so only a brief description will be given here. A thin Pt ribbon filament is used to heat a film of material of about 200  $\mu\text{g}$  mass at  $dT/dt = 2000 \text{ K/s}$  to a constant temperature representative of the surface during steady combustion. This set temperature is maintained while the gaseous products evolve into the cool surrounding atmosphere of an inert gas. These products are monitored several mm above the surface in near real-time by rapid-scan (50–100 ms/scan) FTS-IR spectroscopy. The sequence of formation and identity of the products outline the thermal decomposition pathway of the simulated surface layer. These products react in the multiphase surface zone, the dark zone, and the luminous flame. The change of the control voltage across the Pt filament is measured simultaneously and indicates the sequential endothermicity and exothermicity of this simulated surface reaction layer.

T-jump/FTS-IR spectra of pyrolyzed bulk samples of HMX<sup>5</sup> and RDX<sup>85</sup> verify the essential details of Scheme II, at least to the 25 atm and 700 K limits of study. Consonant with Scheme II, the initially detected thermolysis products are NO<sub>2</sub> and N<sub>2</sub>O, whereas the formation of CH<sub>2</sub>O and HCN is slightly delayed. The overall process is approximately thermally neutral. A second important finding is that the concentration ratio of N<sub>2</sub>O/NO<sub>2</sub> depends on the set temperature.<sup>5</sup> The pattern is shown in Fig. 1. Thus, reaction (6) is favored at lower temperature, whereas reaction (7) is favored at high temperature. This trend is corroborated by lower temperature-lower heating rate experiments, which show that N<sub>2</sub>O and CH<sub>2</sub>O are among the major products.<sup>77</sup> N<sub>2</sub>O is also detected in the cooler subsurface by IR-fiber optic interrogation of a burning propellant composed mostly of RDX.<sup>94</sup> Conversely, high heating rate experiments on HMX, such as those of Morgan and Beyer,<sup>4</sup> reveal H<sub>2</sub>CN and NO<sub>2</sub>, while those of Botcher and Wight<sup>6</sup> on RDX reveal that NO<sub>2</sub> is the only nitrogen oxide cleaved from RDX. The concentration of NO<sub>2</sub> is maximum near the surface of RDX according to uv-visible absorption and planar laser-induced fluorescence (PLIF) measurements at 1 atm by Hanson-Parr and Parr.<sup>95</sup> Despite the qualitative agreements among products, there is no absolute proof that Scheme II is complete. For example, a small amount of CO<sub>2</sub> appears early in the T-jump/FTS-IR measurements,<sup>5</sup> and a

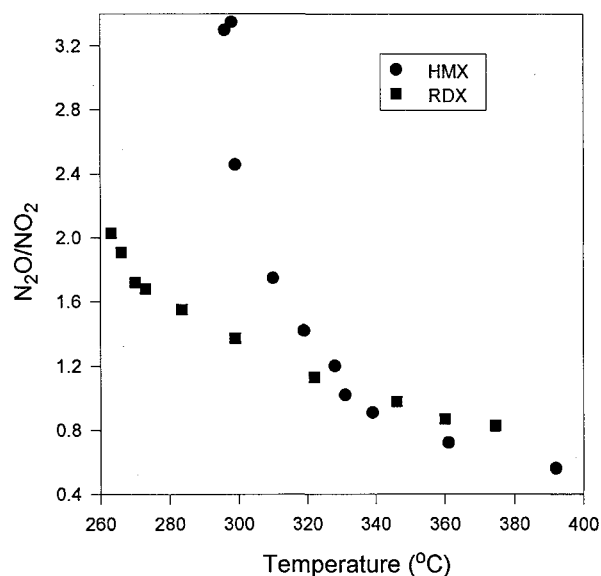


Fig. 1 Experimental N<sub>2</sub>O/NO<sub>2</sub> ratio after 10 s at 5 atm Ar from T-jump/FTIR spectroscopy of HMX and RDX at the temperatures shown. The ratios above 320°C were used and taken to be the same for RDX and HMX within experimental accuracy.

larger amount is found in the time-of-flight (TOF) mass spectrometry data of Fetherolf et al.<sup>55</sup>

Going beyond Scheme II by dividing reactions (6) and (7) into a series of verifiable elementary steps in the multiphase zone of the combustion wave will be very difficult. The fact that  $\text{N}_2\text{O}$  and  $\text{NO}_2$  do not even appear simultaneously with  $\text{CH}_2\text{O}$  and  $\text{HCN}$  is an indication that each product in Scheme II forms by a different step.<sup>5,75,85</sup> Also, substantial evidence is available that H-atom transfer occurs in the rate-determining step of burning RDX and HMX.<sup>96</sup> These facts all indicate that many chemical details are imbedded in this semiglobal description. However, the semiglobal nature of Scheme II must be retained if the combustion description is to rest mostly upon experimental evidence rather than conjecture.

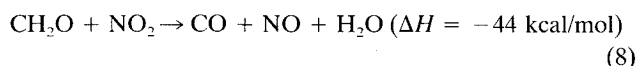
In summary, Scheme II appears to play a major role in the thermal decomposition of the liquid and vapor phases of RDX and HMX at pressures above 1 atm. Competition of Scheme II with several other lesser abundant reactions is not rigorously ruled out. The competition between reactions (6) and (7) in Scheme II depends on temperature, as revealed by Fig. 1. However, Scheme II is approximately thermally neutral so that reactions that generate heat to sustain (6) and (7) must be determined. Several plausible reactions, one of which has been experimentally indicated to involve the interfacial zone, are considered next.

## B. Heat Generation Reactions of HMX and RDX

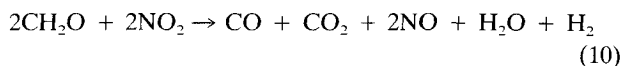
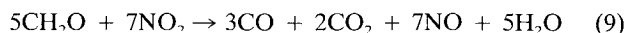
Because Scheme II is experimentally observed to produce little heat,<sup>5</sup> secondary reactions among the products of reactions (6) and (7) must provide the heat to sustain pyrolysis. These reactions can occur in the bulk phase, in bubbles, and on the near-field gaseous side of the surface. Several plausible secondary reactions are considered here:  $\text{CH}_2\text{O} + \text{NO}_2$ ,  $\text{CH}_2\text{O} + \text{N}_2\text{O}$ , and  $\text{HCN} + \text{NO}_2$ . The relative merits of these reactions can be specified by spectroscopic observation and kinetic modeling.

### 1. $\text{CH}_2\text{O} + \text{NO}_2$

By T-jump/FTS-IR spectroscopy, the strong exotherm during decomposition of the molten film of HMX and RDX coincides with the formation of  $\text{NO}$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}$ .<sup>5,85</sup>  $\text{CH}_2\text{O}$  and  $\text{NO}_2$  simultaneously diminish, which is consistent with the occurrence of reaction (8):



This reaction can also be balanced by using additional products as shown in (9)<sup>64</sup> and (10),<sup>87</sup> with somewhat different resulting values of  $\Delta H$ . Reaction (9) differs from (8) by further oxidation of  $\text{CO}$  by  $\text{NO}_2$ . Reaction (10) is unsatisfying chemically because it is like (8), except that  $\text{CO}$  is oxidized by  $\text{H}_2\text{O}$ . The product stoichiometry of (9) is most consistent with T-jump/FTS-IR spectroscopy<sup>5</sup>:



Previous thermolysis<sup>80,82</sup> and controlled atmosphere studies<sup>97</sup> are consistent with (8) and (9). Because of the design of the T-jump/FTS-IR experiment, exothermicity will not be detected unless a large heat transfer coefficient exists between the sample and the filament.<sup>91</sup> This condition exists only if (8) and (9) occur as part of the two-phase zone as opposed to only the near-field gas phase. Several mass spectral and optical determinations of the gaseous products in the near field during the combustion of HMX and RDX qualitatively support Scheme II and reactions (8) and (9).<sup>48,49,53–55,95</sup> For

example, the large quantity of  $\text{NO}$  can be attributed to (8) and (9), while the large quantity of  $\text{HCN}$  and the large  $\text{HCN}/\text{N}_2\text{O}$  ratio in the near-field gaseous regime<sup>47–49,51,53–55,88</sup> are consistent with dominance of reaction (7) over (6) and the occurrence of reactions (8) and (9). The consensus of modeling efforts on HMX and RDX has also been that reactions (8) and (9) play a crucial role in the surface and near-field gaseous zones.<sup>46,50,51,63,64,84,87</sup>

In practice, quantitative specifics of reactions (6–9) are difficult to define when they occur in the two-phase region. Reaction (8) is second-order in the gas phase.<sup>98</sup> Sizable differences exist in the reported Arrhenius parameters for (8),<sup>98–100</sup> which are shown in Table 1. None of these experimentally determined rates were used by Cohen et al.,<sup>47</sup> or Kubota<sup>13</sup> in their descriptions. However, greatest confidence can probably be placed in the kinetic measurements by Lin et al.,<sup>98</sup> because of the wide temperature range over which their mechanistic model seems to apply. Still, these kinetics were determined for the gas phase. The rate is likely to be different when reaction (8) takes place in the condensed phase and at the gas-liquid interface. It is important to have the phase dependence of the rate, which is unknown at this time. The following systematic approach is suggested to scale the rate between phases. If the plausible assumption is made that the mechanism of reaction (8) is similar in the gas, liquid, and gas-liquid interfacial regions, then a kinetic compensation effect should exist in the Arrhenius parameters for these regions.<sup>71</sup> That is, the values of  $E_a$  and  $\ln A$  can be increased or decreased pairwise so that a particular isokinetic temperature is maintained, but the rate at other temperatures or in other phases becomes different. Reaction (8) could be expected to have up to roughly 30% larger Arrhenius parameters in the liquid state than in the vapor state, based on comparison with the global kinetics of decomposition of HMX and RDX.<sup>71</sup>

Finally, the pressure dependence of reaction (8) has not been determined. The effect of pressure on a specific chemical reaction depends on the change of the volume of activation in the rate determining step. This step in the bimolecular reaction (8) is the transfer of H from  $\text{CH}_2\text{O}$  to  $\text{NO}_2$ ,<sup>98</sup> which is likely to have a small volume of activation and, thus, small pressure dependence. However, in the surface reaction zone, reactions (8) and (9) take place as part of a multiphase reaction layer in which  $\text{CH}_2\text{O}$  and  $\text{NO}_2$  continuously form according to Scheme II and are depleted by reactions (8) and (9). In this case, the process is pressure-dependent because the density of  $\text{CH}_2\text{O}$  and  $\text{NO}_2$  in the control volume of the surface and near-field gaseous reaction zones<sup>102</sup> is higher at elevated pressure. It is easiest to account for the effect of pressure on the rate by using the perfect gas law. Equation (11) results, but overestimates the effect at high pressure. As will be discussed in Sec. VIII, reactions (8) and (9) appear to

Table 1 Arrhenius parameters for exothermic reactions

T, K	A, cc/mol s	$E_a$ , kcal/mol	Reference
<b><math>\text{CH}_2\text{O} + \text{NO}_2</math></b>			
>443	$10^{12}$	19.0	99
1424–1910	$10^{13.1}$	26.7	100
300–2000	$8.02 \times 10^{12} T^{2.77}$	13.73	98
<b><math>\text{HCN} + \text{NO}_2</math></b>			
1424–1910	$4.9 \times 10^{11}$	43.3 <sup>a</sup>	100
350–600	$1 \times 10^{12}$	25.0	101
<b><math>\text{CH}_2\text{O} + \text{N}_2\text{O}</math></b>			
1424–1910	$8.41 \times 10^{11}$	27.4 <sup>b</sup>	100

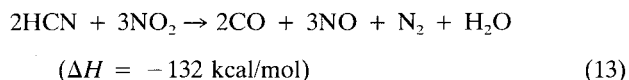
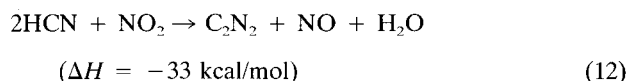
<sup>a</sup>Order is reported to be 1.67. <sup>b</sup>Order is reported to be 1.65.

dominate in producing heat, at least at pressures up to 100 atm and temperatures up to 700–800 K:

$$k = (AP/RT)e^{-E_a/RT} \quad (11)$$

## 2. HCN + NO<sub>2</sub>

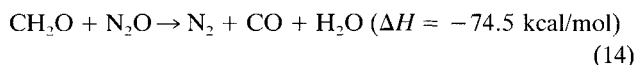
HCN and NO<sub>2</sub> are increasingly preferred decomposition products of HMX and RDX as the temperature increases (Fig. 1). Consequently, reactions (12) and (13)<sup>103</sup> could contribute extensively at higher temperature:



Substantially different rates have been measured for the exothermic reaction of HCN and NO<sub>2</sub> (Table 1). Because of modeling, the kinetic measurement of He et al.<sup>101</sup> is best-supported.

## 3. CH<sub>2</sub>O + N<sub>2</sub>O

In a description of nitramine combustion reactions that predated most of the kinetic measurements in Table 1, McCarty<sup>66</sup> suggested an important role for reaction (14). Knowledge about the products of thermal decomposition of HMX and RDX at the time of McCarty's report came primarily from studies at low heating rates and low temperatures in which CH<sub>2</sub>O and N<sub>2</sub>O are major products:



As noted previously, these products are dominated by HCN and NO<sub>2</sub> under combustion-like conditions.<sup>4–6</sup> The only measured rate constant found for reaction (14) (Table 1) is from Fifer and Holmes,<sup>100</sup> but others subsequently assumed very different rates in combustion models, e.g.,  $k$  (cc/mol·s) =  $1.2 \times 10^{13} \exp(-44,000/RT)$ ,<sup>63</sup> and  $k = 3.2 \times 10^7 \exp(-16,000/RT)$ .<sup>41</sup> Several other models of combustion make use of reaction (14).<sup>13,50</sup> When Hatch allowed reaction (14) to dominate, the burning rate of HMX at 67 atm was twice the experimental value.<sup>50</sup> On the other hand, Ben-Reuven et al.<sup>63</sup> discounted the role of reaction (14).

It should be mentioned that Korobeinichev et al.<sup>53</sup> did not believe that reactions (8–14) [especially (8) and (9)] play as large a role in the near field as the reaction of HCN with NO. Since NO is itself a product of many of the secondary exothermic reactions given above, the HCN + NO reaction would belong to a tertiary class of reactions. The conclusions of Korobeinichev et al.<sup>53</sup> were based largely on quartz microprobe mass spectrometry measurements and modeling of the flame zone of RDX. The inability to probe and separate the most reactive species very close to the surface will tend to skew the description of the chemistry toward a farther field, such as the dark zone, where the reaction of HCN and NO could indeed be quite important.

## VI. Vaporization of Intact HMX and RDX

The equilibrium vapor pressure  $P_v$  above the solid or liquid phase of a pure substance depends on temperature according to the Van't Hoff Eq. (15), where  $\Delta H^\circ$  is the standard heat

$$P_v = P_0 e^{-\Delta H^\circ/RT} \quad (15)$$

of vaporization. The heat of vaporization decreases with increasing temperature and reaches zero at the vapor–liquid critical point. This change of  $\Delta H$  with temperature is not

accounted for by (15), which yields a straight line. Consequently, Eq. (16), which parametrically allows for the change of  $\Delta H$  with temperature, is needed:

$$\Delta H(T) = \Delta H^\circ + aT + bT^2 + cT^3 + \dots \quad (16)$$

Unfortunately, Eq. (16) has not been parameterized for HMX or RDX.

Measurements of the solid-vapor equilibrium ( $\Delta H^\circ_{\text{subl}}$ ) of HMX and RDX<sup>104–108</sup> by Eq. (15) are summarized in Table 2. The vapor pressure for RDX is greater than HMX at a given temperature. No measurements have been reported for the liquid–vapor equilibrium, so that  $\Delta H^\circ_{\text{evap}}$  is commonly extracted from Eq. (17).  $\Delta H^\circ_{\text{melting}}$  for RDX is 8.52 kcal/mol, whereas the value for HMX is estimated to be 11.4 kcal/mol<sup>64</sup>:

$$\Delta H^\circ_{\text{evap}} = \Delta H^\circ_{\text{subl}} - \Delta H^\circ_{\text{melting}} \quad (17)$$

The Arrhenius equation for the rate of vaporization [Eq. (1),  $n = 0$ ] has the same form as Eq. (15). Measurements of the rate vaporization of HMX yield  $E_a = 38$  and 22.9 kcal/mol,<sup>109</sup> but no  $A$  factor was reported. An estimate of  $E_a$  from  $\Delta H^\circ_{\text{subl}}$  gave  $E_a = 39.45$  kcal/mol,<sup>109</sup> although the reasoning is dubious. Melius estimated  $k = 7.5 \times 10^{16} \exp(-22,600/RT) \text{ s}^{-1}$  for the rate of evaporation of RDX in his combustion model.<sup>51</sup> A frequent method to obtain the rate of vaporization has been to use the *prima facie* similarity of the kinetic Eq. (1) and the thermodynamic Eq. (15) and transfer the variables between them.<sup>62–64</sup> In doing so, the approximation is accepted that liquid–vapor equilibrium exists next to the burning surface. However, this is not quite true under combustion conditions because of the high velocity mass flow away from the surface. Furthermore, as was just noted, the value of  $\Delta H^\circ_{\text{evap}}$  changes with temperature. It is only a rough approximation to extrapolate  $\Delta H^\circ_{\text{evap}}$  from the lower temperature range of measurement to the higher temperature range of combustion. Melius<sup>51</sup> used the difference between the rate of evaporation and condensation to obtain the burning rate, while Mitani and Williams<sup>62</sup> used vapor pressure as a means to calculate the surface temperature.

The parameters chosen for Eq. (15) and the pressure and temperature dependence assumed for vaporization affect the division of heat between the gaseous and condensed phases. Although this is an important detail, the influence of evaporation is not considered further here because the focus is on the extensive experimental evidence for both chemical reaction and heat release in the surface layer, at least at pressures below 67 atm.

## VII. Surface Temperature Measurements

The surface temperature  $T_s$  during combustion is most commonly determined by using a microthermocouple imbedded in the material. Various considerations are summarized by

Table 2 Vaporization parameters for RDX and HMX [Eq. (15)]

$T$ , °C	log $A$ , mm Hg	$\Delta H^\circ_{\text{subl}}$ , cal/mol	Reference
RDX			
56–98	14.18	31,110	105
56–140 <sup>a</sup>	14.4 ± 0.6	31,500 ± 500	108
70–174	16.89	32,080	107
110–138	10.87	26,770	104
HMX			
97–129	16.18	41,890	105
97–214 <sup>b</sup>	17.6 ± 1.9	44,300 ± 700	108
142–206	16.86	38,470	107
188–213	14.95 ± 0.23	38,600 ± 1,000	106

<sup>a</sup>Curve fit of data in Refs. 104 and 105.

<sup>b</sup>Curve fit of data in Refs. 105 and 106.

Zanotti et al.<sup>72</sup> Through limited pressure ranges, changes in the ambient pressure cause approximately parallel changes in the burning rate and  $T_s$  by Eq. (2). However, Beckstead noted the poor agreement among the experimentally determined surface temperatures of HMX and the burn rate (Fig. 2).<sup>110</sup> The data of Mitani and Takahashi<sup>111</sup> are the most extensive, but also the most unusual. The lowest regression rates are considerably below the liquefaction temperature of HMX. The temperatures determined by Lengellé and Duterré<sup>112</sup> are consistently higher than those of Kubota and Sakamoto<sup>113</sup> and Parr and Hanson-Parr.<sup>114</sup> Because of the steep temperature gradient at the surface, higher surface temperatures will result if a portion of the flame zone becomes included in the measurement. By excluding the data of Mitani and Takahashi, the three remaining studies are consistent in showing that the surface temperature of burning HMX is in the 650–850 K range at the pressures used. This range is too wide to be of specific value for defining chemical kinetics, but it is qualitatively useful.

Calculated surface temperatures from several combustion models of HMX and RDX are listed in Table 3. The agreement is not much better than in the experimental data, but the expected trend of increasing surface temperature with pressure roughly exists. The lower surface temperatures for RDX compared to HMX have been attributed to the lower heat of vaporization and melting point of RDX.<sup>62</sup>

One might try to estimate the boiling temperature  $T_b$  of RDX and HMX from Trouton's rule, Eq. (18). This estimate

presumes that RDX and HMX boil without decomposition, which is clearly not true. However,  $T_s = T_b$  with this assumption:

$$\Delta H_{\text{evap}}/T_b = x \quad (18)$$

It also requires that the value of  $x$  be known. For nonpolar liquids,  $x = 21$ – $22$  cal/deg mol. For energetic materials exhibiting some association in the liquid state,  $x$  is probably larger. For example,  $x = 23$ – $32$  cal/deg mol for nitroaromatic compounds.<sup>116</sup> A conservative value of  $x = 30$  cal/deg mol was chosen here just to see what Eq. (18) predicts for RDX and HMX.  $\Delta H_{\text{evap}}$  was estimated from Eq. (17) by using the  $\Delta H_{\text{subl}}$  values from Maksimov et al.<sup>108</sup> With these parameters the two additional values of  $T_s$  given in Table 3 are obtained.  $T_s$  for RDX is on the high side of the reasonable range, whereas  $T_s$  for HMX is far too large. These results could be viewed as further evidence that considerable decomposition takes place in the condensed phase of RDX and HMX during combustion, and/or that  $\Delta H_{\text{evap}}$  is smaller in the combustion regime compared to the range in which measurements have been made.

### VIII. Chemical Description of the Surface Reaction Zone

Chemical models of the surface reaction zone, that are couched primarily in experimentally established kinetics, are difficult to validate with measured surface temperatures because of the wide range of available experimental values in Table 3. However, it is possible to estimate the temperature, residence time, and thickness of the surface chemical reaction zone based on kinetics alone. This train of thought concludes this article.

Scheme II and reactions (8–14) frame the chemistry that converts intact HMX and RDX into the heat generation process in the two-phase surface layer defined in Sec. II. The elementary steps, reactive intermediates, and details of homogeneous and heterogeneous processes are not known, but the overall steps can be written to be consistent with the gaseous products detected during simulated and actual combustion. Proceeding on this foundation, reasonable rate constants can be estimated for the decomposition reactions (6) and (7). The rates of (8) and (12), which are strongly exothermic and potentially early stage reactions, then define the fastest rates that are possible at a given temperature and pressure. These predictions can be compared to  $T_s$  values in Table 3 for HMX and RDX, and used to estimate the residence time and the surface layer thickness.

#### A. Rate of Reaction (7)

The rate-determining step of reaction (7) for HMX and RDX is probably  $\text{N-NO}_2$  homolysis, which is the first step during rapid thermal decomposition.<sup>6</sup> The simplest way to estimate this rate is by using the rate of thermal decomposition of dimethylnitramine (DMN). Six mostly gas-phase measurements and one estimate of this rate are given in Table 4.<sup>117–122</sup> These data do not agree, but a kinetic compensation effect exists (Fig. 3). The occurrence of the compensation effect suggests bias in the rate measurements which is probably caused by such factors as differences in experimental conditions, wall reactions, and secondary homogeneous reactions.<sup>71</sup> The thermochemical kinetics estimate<sup>119</sup> and the recent measurement by Lloyd et al.<sup>118</sup> are approximately the average of these data. The rate given by Lloyd et al.<sup>118</sup> was chosen here to represent  $\text{N-NO}_2$  homolysis. For statistical reasons the value of  $A$  was increased by a factor of 3 for RDX, and 4 for HMX yielding (19) and (20):

$$k_7(\text{RDX}) = 10^{16.4} \exp(-44,100/RT) \text{ s}^{-1} \quad (19)$$

$$k_7(\text{HMX}) = 10^{16.5} \exp(-44,100/RT) \text{ s}^{-1} \quad (20)$$

Table 3 Calculated surface temperatures  $T_s$

P, atm	$T_s$ , K		Reference
	RDX	HMX	
0.5	593	—	53
1	549	—	51
1	550	—	115
1	560	680	2
1	690	—	62
1	766	1097	Eq. (18) <sup>a</sup>
20	643	—	51
68	—	874	70
100	630	—	115
100	710	870	2
100	870	—	62

<sup>a</sup>Trouton's rule estimate assuming no reaction in the surface layer and  $\Delta H_{\text{evap}}$  measured at a much lower temperature.

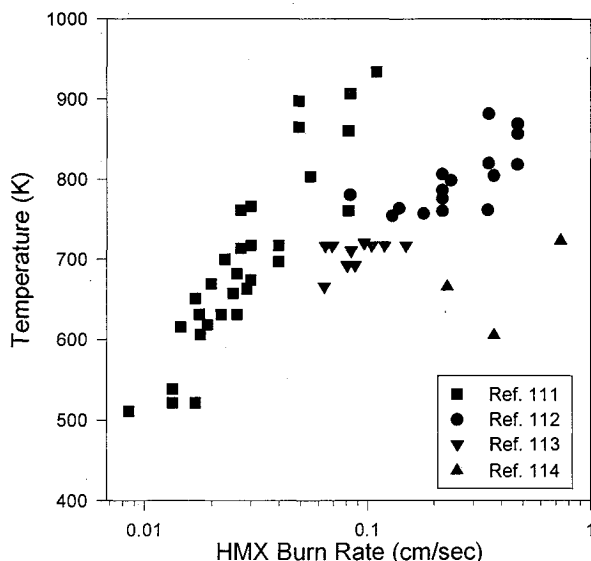


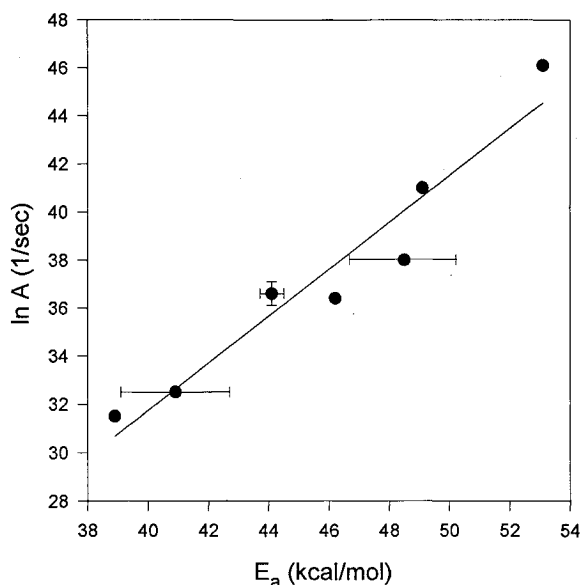
Fig. 2 Surface temperature measurements for HMX.



**Table 4** Arrhenius parameters for N-NO<sub>2</sub> homolysis of DMN

A, s <sup>-1</sup>	E <sub>a</sub> , cal/mol	Reference
10 <sup>13.7</sup>	38,900	117
10 <sup>14.1</sup>	40,700 ± 1,800	117
10 <sup>15.9 ± 0.2</sup>	43,700 ± 400	118
10 <sup>15.8</sup>	46,200 <sup>a</sup>	119
10 <sup>16.5</sup>	48,500 ± 1,800	120
10 <sup>17.8</sup>	48,100 <sup>b</sup>	121
10 <sup>20</sup>	53,100	122

<sup>a</sup>Thermochemical kinetics estimate. <sup>b</sup>In isooctane solution.

**Fig. 3** Kinetic compensation effect that exists in the thermal decomposition rate measurements on dimethylnitramine.**B. Rate of Reaction (6)**

N<sub>2</sub>O and CH<sub>2</sub>O form separately from a complex set of reactions.<sup>5</sup> No simple secondary nitramine is known that forms only N<sub>2</sub>O and CH<sub>2</sub>O in order that the rate can be determined. However, the rate can be estimated by using the rate of reaction (7) [Eqs. (19) and (20)], and the temperature dependence of the N<sub>2</sub>O/NO<sub>2</sub> concentration ratio in Fig. 1. The N<sub>2</sub>O/NO<sub>2</sub> ratio should closely track  $k_7/k_6$ , because N<sub>2</sub>O and NO<sub>2</sub> are unique to reactions (6) and (7). Figure 1 shows that above 330°C, the N<sub>2</sub>O/NO<sub>2</sub> concentration ratio for HMX and RDX is the same within experimental error. By fixing the rate of (7) according to Eqs. (19) and (20), the “best fit” Arrhenius constants for reaction (6) can be determined by curve-fitting the ratio in Fig. 1. The rates given by Eqs. (21) and (22) result. These rates broadly agree with those of primary nitramines that thermolyze to N<sub>2</sub>O, an aldehyde, and H<sub>2</sub>O.<sup>123</sup> Methylene dinitramine<sup>124</sup> affords  $E_a = 35.4$  kcal mol<sup>-1</sup> and  $A = 10^{15.6}$  s<sup>-1</sup>, while ethylenedinitramine<sup>125</sup> yields  $E_a = 30.5$  kcal/mol and  $A = 10^{12.8}$  s<sup>-1</sup>.

The rates given by Eqs. (19–22) define the initial distribution of products from reactions (6) and (7) for RDX and

$$k_6(\text{RDX}) = 10^{12.9} \exp(-34,400/RT) \text{ s}^{-1} \quad (21)$$

$$k_6(\text{HMX}) = 10^{13.0} \exp(-34,400/RT) \text{ s}^{-1} \quad (22)$$

HMX at least up to about the temperature of the burning surface. The pressure dependence of these rates is expected to be small because the reactions occur primarily in the condensed phase. However, the product distribution is indirectly

affected by pressure because  $T_b$  changes with pressure. The products of reactions (6) and (7) are the main reactants for the primary flame zone and are a powerful source of heat.

**C. Rates of Primary Exothermic Reactions**

As discussed in Sec. V.B., the reaction between CH<sub>2</sub>O and NO<sub>2</sub> is indicated by T-jump/FTS-IR spectroscopy to be the first strongly exothermic reaction for RDX and HMX. This reaction can occur in the condensed phase, in bubbles and voids in the liquid layer, and in the gas phase near the surface. Rate measurements of this reaction are summarized in Table 1. However, this nominally gas-phase bimolecular reaction is expected to be sensitive to pressure. Therefore, Eq. (11) was used to describe the contribution of reaction (8).

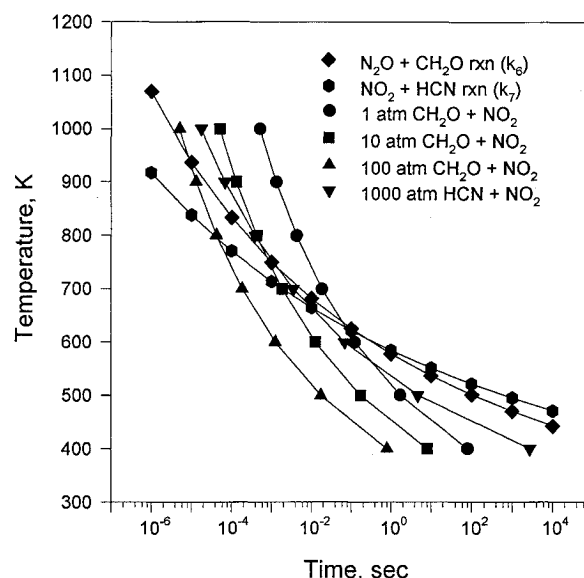
Although the reaction between HCN and NO<sub>2</sub> [reactions (12) and (13)] was not indicated by T-jump/FTS-IR spectroscopy (no C<sub>2</sub>N<sub>2</sub> was observed), HCN and NO<sub>2</sub> become increasingly preferred products as the temperature increases. Consequently, the higher initial concentrations of HCN and NO<sub>2</sub> enhance the potential contribution of (12) and (13) at higher pressure and temperature.

**D. Composite Chemistry Description of the Surface Zone**

The rearranged version of the Arrhenius Eq. (23) is especially helpful for visualizing combustion and explosion chemistry.<sup>126</sup> The time constant or residence time for essentially complete reaction  $\Delta t$ , rather than the rate constant, can be plotted vs temperature. For a pressure dependent process

$$T_{\text{reaction}} = \frac{E_a}{R(\ln A + \ln \Delta t)} \quad (23)$$

such as the one that occurs with the CH<sub>2</sub>O + NO<sub>2</sub> and HCN + NO<sub>2</sub> reactions, Eq. (23) is modified with Eq. (11). Of course, the effect at high pressure is given only qualitatively. Figure 4 for HMX is a plot of Eq. (23) for reactions (6) and (7) and reactions (8) and (12) using Eq. (23) modified by Eq. (11). Focusing on reactions (6) and (7) first, (6) is faster than (7) at temperatures below about 600 K. Above 600 K, reaction (7) is faster. Extrapolation of these rates to higher temperatures is dubious, but they are probably reasonable estimates to about 800 K. At this temperature, reaction (7) clearly dominates in accordance with flash pyrolysis data.<sup>6</sup> The decomposition process of HMX and RDX becomes increasingly endothermic to the extent that reaction (7) dominates.

**Fig. 4** Plots of Eqs. (11) and (23) for the reactions of HMX indicated.  $\Delta t$  is the residence time of the surface zone at a given temperature  $T$ .



**Table 5 Predicted surface reaction zone characteristics of HMX and RDX**

$P$ , atm	$\dot{r}$ , cm/s <sup>a</sup>	$T_s$ , <sup>b</sup> K	$\Delta t$ , <sup>b</sup> ms	$h$ , $\mu\text{m}$ <sup>c</sup>
1	0.063	~620	100	63
10	0.63	~710	1	6
100	6.3	~800	0.1	6

<sup>a</sup>Reference 113. <sup>b</sup>From Fig. 4. <sup>c</sup>From  $\dot{r}$  and residence time [Eq. (24)].

The secondary reactions among the products of (6) and (7) produce the heat needed to sustain (6) and (7). These secondary exothermic reactions must occur at a faster rate than (6) or (7) for a given temperature. Otherwise the decomposition of RDX or HMX will cease. The behavior of the  $\text{CH}_2\text{O} + \text{NO}_2$  reaction at 1, 10, and 100 atm is shown. The reaction time of decomposition of HMX and RDX via (6) and (7) must be longer than (to the right of) the  $\text{CH}_2\text{O} + \text{NO}_2$  reaction time, in order for  $\text{CH}_2\text{O} + \text{NO}_2$  to be the source of heat. The temperature at which the secondary exothermic reaction is complete sets an upper limit on  $T_s$  in this simple description of the multiphase surface zone. Reading from Fig. 4, the temperature required for completion of reactions (6) and (7) first, and then followed by (18) at 1 atm is about 620 K, and the residence time for complete reaction is about 100 ms. At 10 atm the surface temperature is roughly 710 K and the residence time is about 1 ms. At 100 atm an interesting situation arises. The surface temperature predicted from the  $\text{CH}_2\text{O} + \text{NO}_2$  reaction is about 800 K, at which temperature reaction (7) will greatly dominate (6). In this case the reaction of  $\text{HCN} + \text{NO}_2$  [Eqs. (12) and (13)] might become a significant source of heat. The tentatively known rate of the  $\text{HCN} + \text{NO}_2$  reaction<sup>100</sup> scaled to 1000 atm is shown on Fig. 4. These rates place it slower than the  $\text{CH}_2\text{O} + \text{NO}_2$  reaction at the same pressure and temperature. Taken together when driven by completion of these reactions,  $T_s$  remains at or below about 800 K. This temperature range is reasonable based on the discussion in Sec. VII.

The thickness of the surface reaction zone  $h$  can be estimated from the residence time  $\Delta t$  in Fig. 4. In doing so remember that the surface reaction zone was defined in Sec. II to include both the two-phase liquid layer and the increment of the near-field gas phase that incorporates the microscopic surface roughness. Table 5 summarizes the predicted surface layer thickness for reactions (6), (7), and (8), and burn rate data for HMX from Parr and Parr.<sup>114</sup> Equation (24) was used for these estimates:

$$\dot{r}\Delta t = h \quad (24)$$

The thickness of the surface zone levels out at about 6  $\mu\text{m}$  in the 10–100 atm range, because the burn rate increases and residence time decreases to compensate for one another.

This description of the surface reaction zone is based entirely on the competition of the rates of a few reactions. The approach is offered as a means of evaluating chemical processes that are difficult or impossible to measure directly in a multiphase layer. It would be naive to imply that these reactions can account for every detail. For example, the role of vaporization is currently neglected, as is the assessment of the heat balance from these three reactions. Other secondary and tertiary gas-phase reactions (e.g.,  $\text{NO} + \text{HCN}$ ) are not included. The rate of  $\text{HCN} + \text{NO}_2$  is still not firmly settled, which adds to further uncertainty about the higher temperature and pressure range. On the other hand, plausible characteristics of the surface layer are predicted by the use of only three competing, experimentally based reactions. Future work remains to refine this description, and to learn more about the changes that take place when an additional component, such as a binder, is present.

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## References

- <sup>1</sup>Alexander, M. H., Dagdigian, P. J., Jacox, M. E., Kolb, C. E., Melius, C. F., Rabitz, H., Smooke, M. D., and Tsang, W., "Nitramine Propellant Ignition and Combustion Research," *Progress in Energy and Combustion Science*, Vol. 17, 1991, pp. 263–296.
- <sup>2</sup>Li, S. C., Williams, F. A., and Margolis, S. B., "Effects of Two-Phase Flow in a Model of Nitramine Deflagration," *Combustion and Flame*, Vol. 80, 1990, pp. 329–349.
- <sup>3</sup>Huang, T. H., Thynell, S. T., and Kuo, K. K., "Partially Confined Hot Fragment Conductive Ignition: Part I—Modeling," Thirtieth JANNAF Combustion Meeting, Monterey, CA, Nov. 1993.
- <sup>4</sup>Morgan, C. U., and Beyer, R. A., "Electron Spin Resonance Studies of HMX Pyrolysis Products," *Combustion and Flame*, Vol. 36, 1979, pp. 99–101.
- <sup>5</sup>Brill, T. B., and Brush, P. J., "Condensed Phase Chemistry of Explosives and Propellants at High Temperature: HMX, RDX, and BAMO," *Philosophical Transactions of the Royal Society of London, Series A: Mathematical and Physical Sciences*, Vol. 339, 1992, pp. 377–385.
- <sup>6</sup>Botcher, T. R., and Wight, C. A., "Transient Thin Film Laser Pyrolysis of RDX," *Journal of Physical Chemistry*, Vol. 97, 1993, pp. 9149–9153; also "Explosive Thermal Decomposition Mechanism of RDX," *Journal of Physical Chemistry*, Vol. 98, 1994, pp. 5441–5444.
- <sup>7</sup>Rice, O. K., and Ginell, R., "The Theory of the Burning of Double Base Rocket Powders," *Journal of Physical and Colloid Chemistry*, Vol. 54, 1950, pp. 885–917.
- <sup>8</sup>Parr, R. G., and Crawford, B. L., Jr., "The Physical Theory of Burning of Double Base Rocket Propellants, I," *Journal of Physical and Colloid Chemistry*, Vol. 54, 1950, pp. 929–954.
- <sup>9</sup>Wilfong, R. E., Penner, S. S., and Daniels, F., "A Hypothesis for Propellant Burning," *Journal of Physical and Colloid Chemistry*, Vol. 54, 1950, pp. 863–872.
- <sup>10</sup>Taylor, J. W., "A Melting Stage in the Burning of Solid Secondary Explosives," *Combustion and Flame*, Vol. 6, 1962, pp. 103–107.
- <sup>11</sup>Parr, T. P., and Hanson-Parr, D. M., "Nitramine Flame Structure as a Function of Pressure," *Proceedings of the 26th JANNAF Combustion Meeting*, Vol. I, CPIA Publ. 529, 1989, pp. 27–37.
- <sup>12</sup>Boggs, T. L., Derr, R. L., and Beckstead, M. W., "The Surface Structure of Ammonium Perchlorate Composite Propellants," *AIAA Journal*, Vol. 8, 1970, pp. 370–372.
- <sup>13</sup>Kubota, N., *Survey of Rocket Propellants and Their Combustion Characteristics*, edited by K. K. Kuo and M. Summerfield, Vol. 90, Progress in Astronautics and Aeronautics, AIAA, New York, 1984, pp. 1–52.
- <sup>14</sup>Kuo, K. K., *Principles of Combustion*, Wiley, New York, 1986.
- <sup>15</sup>Zenin, A. A., *Thermophysics of Stable Combustion Waves*, Vol. 143, Progress in Astronautics and Aeronautics, AIAA, Washington, DC, 1992, pp. 197–231.
- <sup>16</sup>Hermance, C. E., "A Model of Composite Propellant Combustion Including Surface Heterogeneity and Heat Generation," *AIAA Journal*, Vol. 4, 1966, pp. 1629–1637.
- <sup>17</sup>Karpowicz, R. J., and Brill, T. B., "In Situ Characterization of the 'Melt' Phase of RDX and HMX by Rapid-Scan FTIR Spectroscopy," *Combustion and Flame*, Vol. 56, 1984, pp. 317–325.
- <sup>18</sup>Kraeutle, K. J., "Thermal Decomposition of HMX: Effect of Experimental Conditions and of Additives," *18th JANNAF Combustion Meeting*, Vol. II, CPIA Publ. 347, 1981, pp. 383–394.
- <sup>19</sup>Batten, J. J., and Murdie, D. C., "Decomposition of RDX at Temperatures Below the Melting Point," *Australian Journal of Chemistry*, Vol. 25, 1972, pp. 2337–2351.
- <sup>20</sup>Hall, P. G., "Thermal Decomposition and Phase Transitions in Solid Nitramines," *Transactions of the Faraday Society*, Vol. 67, 1971, pp. 556–562.
- <sup>21</sup>Barrere, M., Jaumotte, A., Venbeke, B. F., and Vandenkerckhove, J., *Rocket Propulsion*, Elsevier, New York, 1960.
- <sup>22</sup>Penner, S. S., *Chemical Rocket Propulsion and Combustion Re-*

search, Gordon and Breach, New York, 1962.

<sup>23</sup>Williams, F. A., Barrere, M., and Huang, N. C., "Fundamental Aspects of Solid Propellant Rockets," AGARDograph 116, Technivision, Slough, England, UK, 1969, pp. 395–456.

<sup>24</sup>Beckstead, M. W., and McCarty, K. P., "Calculated Combustion Characteristics of Nitramine Monopropellants," *13th JANNAF Combustion Meeting*, Vol. I, 1976, pp. 57–68.

<sup>25</sup>Kishore, K., "Comprehensive View of the Combustion Models of Composite Solid Propellants," *AIAA Journal*, Vol. 17, 1979, pp. 1216–1224.

<sup>26</sup>Cohen, N. S., "Review of Composite Propellant Burn Rate Modeling," *AIAA Journal*, Vol. 18, 1980, pp. 277–293.

<sup>27</sup>Ramohalli, K. N. R., "Steady State Burning of Composite Propellants Under Zero Cross-Flow Situation," Vol. 90, *Progress in Astronautics and Aeronautics*, AIAA, New York, 1984, pp. 409–478.

<sup>28</sup>Lewis, B., and Von Elbe, G., "On the Theory of Flame Propagation," *Journal of Chemical Physics*, Vol. 2, 1934, pp. 537–546.

<sup>29</sup>Zeldovich, Ya. B., "Theory of Burning of Powders and of Explosive Substances," *Journal of Experimental and Theoretical Physics (USSR)*, Vol. 12, 1942, pp. 498–524.

<sup>30</sup>Belyaev, A. F., "Combustion of Explosives," *Acta Physical Chemistry URSS*, Vol. 8, 1938, pp. 763–772.

<sup>31</sup>Summerfield, M., Sutherland, G. S., Webb, M. J., Taback, H. J., and Hall, K. P., "Burning Mechanism of Ammonium Perchlorate Propellants," *Solid Propellant Rocket Research*, Academic, New York, 1960, pp. 141–182.

<sup>32</sup>Blair, D. W., Bastress, E. K., Hermance, C. E., Hall, K. P., and Summerfield, M., "Some Problems in Steady-State Burning of Composite Solid Propellants," *Solid Propellant Rocket Research*, Academic, New York, 1960, pp. 183–206.

<sup>33</sup>Beckstead, M. W., Derr, R. L., and Price, C. F., "A Model of Composite Solid Propellant Combustion Based on Multiple Flames," *AIAA Journal*, Vol. 8, 1970, pp. 2200–2207.

<sup>34</sup>Beckstead, M. W., Derr, R. L., and Price, C. F., "The Combustion of Solid Monopropellants and Composite Propellants," *Thirteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1970, pp. 1047–1056.

<sup>35</sup>Guirao, C., and Williams, F. A., "A Model for Ammonium Perchlorate Deflagration Between 20 and 100 Atm," *AIAA Journal*, Vol. 9, 1971, pp. 1345–1356.

<sup>36</sup>Glick, R. L., "On Statistical Analysis of Composite Solid Propellant Combustion," *AIAA Journal*, Vol. 12, 1974, pp. 384, 385.

<sup>37</sup>Condon, J. A., and Osborn, J. R., "The Effect of Oxidizer Particle Size Distribution on the Steady and Non-Steady Combustion of Composite Propellants," Air Force Rocket Propulsion Lab., AFRPL-TR-78-17, Edwards AFB, CA, June 1978; also Miller, R. R., "A Framework for a Totally Statistical Composite Propellant Combustion Model," *19th JANNAF Combustion Meeting*, Oct. 1982.

<sup>38</sup>Miller, M. S., "In Search of an Idealized Model of Homogeneous Solid Propellant Combustion," *Combustion and Flame*, Vol. 46, 1982, pp. 51–73.

<sup>39</sup>Ermolin, N. E., Korobeinichev, O. P., Tereshchenko, A. G., and Fomin, V. M., "Kinetic Calculations and Mechanism Definition for Reactions in an Ammonium Perchlorate Flame," *Fizika Goreniya i Vzryva*, Vol. 18, 1982, pp. 180–189.

<sup>40</sup>Sahu, H., Sheshadri, T. S., and Jain, V. K., "Novel Kinetic Scheme for the Ammonium Perchlorate Gas Phase," *Journal of Physical Chemistry*, Vol. 94, 1990, pp. 294, 295.

<sup>41</sup>Cohen, N., "A Review of Kinetic Models of the High Temperature Gas Phase Decomposition of Ammonium Perchlorate," Aerospace Corp., ATR-92(9558)-3, Los Angeles, CA, 1992.

<sup>42</sup>Brill, T. B., Brush, P. J., and Patil, D. G., "Thermal Decomposition of Energetic Materials 60. Major Reaction Stages of a Simulated Burning Surface of  $\text{NH}_4\text{ClO}_4$ ," *Combustion and Flame*, Vol. 94, 1993, pp. 70–76.

<sup>43</sup>Price, C. F., Boggs, T. L., and Derr, R. L., "Modeling of Solid Monopropellant Deflagration," *AIAA Paper 78-219*, Jan. 1978.

<sup>44</sup>Price, C. F., Boggs, T. L., and Derr, R. L., "The Steady-State Combustion Behavior of Ammonium Perchlorate and HMX," *AIAA Paper 79-0164*, Jan. 1979.

<sup>45</sup>Beckstead, M. W., "A Model for Solid Propellant Combustion," *Eighteenth Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1981, pp. 175–183.

<sup>46</sup>Bizot, A., and Beckstead, M. W., "A Model for HMX Propellant Combustion," *Flame Structure*, edited by O. P. Korobeinichev, Vol. 1, Nauka Siberian Branch, Novosibirsk, USSR, 1991, pp. 230–235.

<sup>47</sup>Cohen, N. S., Lo, G. A., and Crowley, J. C., "Model and Chemistry of HMX Combustion," *AIAA Journal*, Vol. 23, 1985, pp. 276–

282.

<sup>48</sup>Ermolin, N. E., Korobeinichev, O. P., Kuibida, L. V., and Fomin, V. M., "Study of the Kinetics and Mechanism of Chemical Reactions in Hexogen Flames," *Fizika Goreniya i Vzryva*, Vol. 22, 1986, pp. 54–64.

<sup>49</sup>Ermolin, N. E., Korobeinichev, O. P., Kuibida, L. V., and Fomin, V. M., "Processes in Hexogene Flames," *Fizika Goreniya i Vzryva*, Vol. 24, 1988, pp. 21–29.

<sup>50</sup>Hatch, R. L., "Chemical Kinetics Modeling of HMX Combustion," *24th JANNAF Combustion Meeting*, Vol. I, CPIA Publ. 476, 1987, pp. 383–391.

<sup>51</sup>Melius, C. F., "Thermochemical Modeling II. Application to Ignition and Combustion of Energetic Materials," *Chemistry and Physics of Energetic Materials*, edited by S. Bulusu, Kluwer, Dordrecht, The Netherlands, 1990, pp. 51–78.

<sup>52</sup>Yetter, R. A., and Dryer, F. L., "RDX Flame Structure," *JANNAF Workshop on Kinetics and Related Aspects of Propellant Combustion Chemistry*, Langley, VA, Oct. 1992.

<sup>53</sup>Korobeinichev, O. P., et al., "Mass Spectrometric Probe Study of the Flame Structure and Kinetics of Chemistry Reactions in Flames," *Mass-Spectrometry and Chemical Kinetics*, Nauka, Moscow, 1985, pp. 73–93.

<sup>54</sup>Trubert, J. F., "Analysis of the Condensed Phase Degradation Gases of Energetic Binders," *AGARD/PEP Specialists' Meeting on Smokeless Propellants*, AGARD C. P. 391, Florence, Italy, Sept. 1985.

<sup>55</sup>Fetherolf, B. L., Liiva, P. M., Litzinger, T. A., and Kuo, K. K., "Thermal and Chemical Structure of the Preparation and Reaction Zones for RDX and RDX Composite Propellants," *28th JANNAF Combustion Meeting*, Vol. II, CPIA Publ. 573, Oct. 1991, pp. 379–386.

<sup>56</sup>Kubota, N., "Combustion Mechanisms of Nitramine Composite Propellants," *Eighteenth Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1981, pp. 187–194.

<sup>57</sup>Hsieh, W. H., Li, W. Y., and Yim, Y. J., "Combustion Behavior and Thermochemical Properties of RDX-Based Solid Propellants," *AIAA Paper 92-3628*, 1992.

<sup>58</sup>Kishore, K., and Gayathri, V., "Chemistry of Ignition and Combustion of Ammonium Perchlorate-Based Propellants," edited by K. K. Kuo and M. Summerfield, Vol. 90, *Progress in Astronautics and Aeronautics*, AIAA, New York, 1984, pp. 53–119.

<sup>59</sup>Krishnan, S., and Jeenu, R., "Subatmospheric Burning Characteristics of AP/CTPB Composite Propellants with Burning Rate Modifiers," *Combustion and Flame*, Vol. 80, 1990, pp. 1–6.

<sup>60</sup>Merzhanov, A. G., "The Theory of Stable Homogeneous Combustion of Condensed Substances," *Combustion and Flame*, Vol. 13, 1969, pp. 143–156.

<sup>61</sup>Manelis, G. B., and Strunin, V. A., "The Mechanism of Ammonium Perchlorate Burning," *Combustion and Flame*, Vol. 17, 1971, pp. 69–78.

<sup>62</sup>Mitani, T., and Williams, F. A., "A Model for the Deflagration of Nitramines," *Twenty-First Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1986, pp. 1965–1974.

<sup>63</sup>Ben-Reuven, M., Caveny, L. H., Vichnevetsky, R. J., and Summerfield, M., "Flame Zone and Sub-Surface Reaction Model for Deflagrating RDX," *Sixteenth Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1976, pp. 1223–1233.

<sup>64</sup>Ben-Reuven, M., and Caveny, L. H., "Nitramine Flame Chemistry and Deflagration Interpreted in Terms of a Flame Model," *AIAA Journal*, Vol. 19, 1979, pp. 1276–1285.

<sup>65</sup>Brill, T. B., "Structure-Thermolysis Relationships for Energetic Materials," *Chemistry and Physics of Energetic Materials*, edited by S. Bulusu, Kluwer, Dordrecht, The Netherlands, 1990, pp. 277–326.

<sup>66</sup>McCarty, K. P., "HMX Propellant Combustion Studies," Air Force Rocket Propulsion Lab., AFRPL-TR-76-59, Edwards AFB, CA, 1976.

<sup>67</sup>Fifer, R. A., "Chemistry of Nitrate Ester and Nitramine Propellants," edited by K. K. Kuo and M. Summerfield, Vol. 90, *Progress in Astronautics and Aeronautics*, AIAA, New York, 1984, pp. 177–237.

<sup>68</sup>Merzhanov, A. G., and Dubovitskii, F. I., "On the Theory of Steady State Monopropellant Combustion," *Proceedings of the USSR Academy Sciences*, Vol. 129, 1959, pp. 153–156.

<sup>69</sup>Lengellé, G., "Thermal Degradation Kinetics and Surface Pyrolysis of Vinyl Polymers," *AIAA Journal*, Vol. 8, 1970, pp. 1989–1996.

<sup>70</sup>Beckstead, M. W., "Modeling AN, AP, HMX, and Double-Base Monopropellants," *26th JANNAF Combustion Meeting*, Vol. 4, CPIA Publ. 529, 1989, pp. 255–286.

- <sup>71</sup>Brill, T. B., Gongwer, P. E., and Williams, G. K., "Thermal Decomposition of Energetic Materials 66. Kinetic Compensation Effects in HMX, RDX, and NTO," *Journal of Physical Chemistry*, Vol. 98, 1994, pp. 12,242–12,247.
- <sup>72</sup>Zanotti, C., Volpi, A., Bianchessi, M., and De Luca, L., "Measuring Thermodynamic Properties of Burning Propellants," Vol. 143, Progress in Astronautics and Aeronautics, AIAA, Washington, DC, 1992, pp. 145–196.
- <sup>73</sup>Adams, G. F., and Shaw, R. W., Jr., "Fast Chemical Reactions in Energetic Materials," *Annual Review of Physical Chemistry*, Vol. 43, 1992, pp. 311–340.
- <sup>74</sup>Schroeder, M. A., "Critical Analysis of Nitramines Decomposition Data: Product Distributions from HMX and RDX Decomposition," Ballistic Research Lab., BRL-TR-2659, Aberdeen Proving Ground, MD, June 1985.
- <sup>75</sup>Behrens, R., Jr., "Thermal Decomposition of Energetic Materials: Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed Phase Decomposition of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine," *Journal of Physical Chemistry*, Vol. 94, 1990, pp. 6706–6718.
- <sup>76</sup>Behrens, R., Jr., and Bulusu, S., "Thermal Decomposition of Energetic Materials 2. Deuterium Isotope Effect and Isotopic Scrambling in Condensed-Phase Decomposition of Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine," *Journal of Physical Chemistry*, Vol. 95, 1991, pp. 5838–5845.
- <sup>77</sup>Behrens, R., Jr., and Bulusu, S., "Thermal Decomposition of Energetic Materials 3. Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed Phase Decomposition of 1,3,5-Trinitrohexahydro-s-Triazine," *Journal of Physical Chemistry*, Vol. 96, 1992, pp. 8877–8891.
- <sup>78</sup>Behrens, R., Jr., and Bulusu, S., "Thermal Decomposition of Energetic Materials 4. Deuterium Isotope Effects and Isotopic Scrambling (H/D, <sup>13</sup>C/<sup>18</sup>O, and <sup>14</sup>N/<sup>15</sup>N) in Condensed Phase Decomposition of 1,3,5-Trinitrohexahydro-s-Triazine," *Journal of Physical Chemistry*, Vol. 96, 1992, pp. 8891–8897.
- <sup>79</sup>Axworthy, A. E., Flanigan, D. A., and Gray, J. C., "Interaction of Reaction Kinetics and Nitramine Combustion," Air Force Armament Lab., AFATL-TR-80-58, Eglin AFB, FL, May 1980.
- <sup>80</sup>Oyumi, Y., and Brill, T. B., "Thermal Decomposition of Energetic Materials 3. High-Rate, In Situ, FTIR of the Thermolysis of RDX and HMX with Pressure and Heating Rate as Variables," *Combustion and Flame*, Vol. 62, 1985, pp. 213–224.
- <sup>81</sup>Suryanarayana, B., and Graybush, R. J., "Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX): A Mass Spectrometric Study of the Products from  $\beta$ -HMX," *Proceedings of the 39th Congress on Industrial Chemistry*, Supplement 24, 1966, pp. 1–4.
- <sup>82</sup>Cosgrove, J. D., and Owen, A. J., "Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)—Part I: The Products and Physical Parameters," *Combustion and Flame*, Vol. 22, 1974, pp. 13–18.
- <sup>83</sup>Cosgrove, J. D., and Owen, A. J., "Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX)—Part II: Effects of the Products," *Combustion and Flame*, Vol. 22, 1974, pp. 19–22.
- <sup>84</sup>Kubota, N., and Sakamoto, N., "Combustion Mechanism of HMX," *Propellants, Explosives, Pyrotechnics*, Vol. 14, 1989, pp. 6–11.
- <sup>85</sup>Brill, T. B., Brush, P. J., Patil, D. G., and Chen, J. K., "Chemical Pathways at a Burning Surface," *Twenty-Fourth Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1992, pp. 1907–1914.
- <sup>86</sup>Edwards, T., "Investigation of Solid Propellant Combustion Chemistry," AIAA Paper 90-0547, Jan. 1990.
- <sup>87</sup>Lengellé, G., Duterque, J. R., Gordon, J. C., and Trubert, J. F., "Solid Propellant Steady Combustion-Physical Aspects," *Journal of Propulsion and Power* (to be published).
- <sup>88</sup>Parr, T. P., and Hanson-Parr, D. M., "Nonintrusive Diagnostic Techniques for Research on Nonsteady Burning of Solid Propellants," Vol. 143, Progress in Astronautics and Aeronautics, AIAA, Washington, DC, 1992, pp. 261–324.
- <sup>89</sup>Stufflebeam, J. H., "CARS Diagnostics for Solid Propellant Combustion Investigations," United Technologies Research Center, R92-957787F, East Hartford, CT, Jan. 1992.
- <sup>90</sup>Vanderhoff, J. A., "Species Profiles in Solid Propellant Flames Using Absorption and Emission Spectroscopy," *Combustion and Flame*, Vol. 84, 1991, pp. 73–92.
- <sup>91</sup>Brill, T. B., Brush, P. J., James, K. J., Shepherd, J. E., and Pfeiffer, K. J., "T-Jump/FTIR Spectroscopy: A New Entry into the Rapid, Isothermal Pyrolysis Chemistry of Solid and Liquids," *Applied Spectroscopy*, Vol. 46, 1992, pp. 900–911.
- <sup>92</sup>Timken, M. D., Chen, J. K., and Brill, T. B., "Thermal Decomposition of Energetic Materials 37. SMATCH/FTIR (Simultaneous Mass and Temperature Change/FTIR) Spectroscopy," *Applied Spectroscopy*, Vol. 44, 1990, pp. 701–706.
- <sup>93</sup>Shepherd, J. E., and Brill, T. B., "Interpretation of Time-to-Explosion Tests," *Tenth Symposium (International) on Detonation* (to be published).
- <sup>94</sup>Wormhoudt, J., Kebabian, P. L., and Kolb, C. E., "Infrared Fiber-Optic Diagnostic Observations of Solid Propellant Combustion," Aerodyne Research, Inc., ARI-RR-1029, Cheyenne, WY, Oct. 1993.
- <sup>95</sup>Hanson-Parr, D., and Parr, T., "RDX Flame Structure and Chemistry," 30th JANNAF Combustion Subcommittee Meeting, Nov. 1993.
- <sup>96</sup>Trulove, P. C., Chapman, R. D., and Shackelford, S. A., "Kinetic Deuterium Isotope Effects in the Combustion of Formulated Nitramine Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 19, 1994, pp. 42–58.
- <sup>97</sup>Palopoli, S. F., and Brill, T. B., "Thermal Decomposition of Energetic Materials 52. On the Foam Zone and Surface Chemistry of Rapidly Decomposing HMX," *Combustion and Flame*, Vol. 87, 1991, pp. 45–60.
- <sup>98</sup>Lin, C. Y., Wang, H. I., Lin, M. C., and Williams, C. F., "A Shock Tube Study of the  $\text{CH}_2\text{O} + \text{NO}_2$  Reaction at High Temperatures," *International Journal of Chemical Kinetics*, Vol. 22, 1990, pp. 455–482.
- <sup>99</sup>Pollard, F. H., and Wyatt, R. M. H., "Reactions Between Formaldehyde and Nitrogen Dioxide," *Transactions of the Faraday Society*, Vol. 45, 1949, pp. 760–767.
- <sup>100</sup>Fifer, R. A., and Holmes, H. E., "Kinetics of Nitramine Flame Reactions," *Sixteenth JANNAF Combustion Meeting*, Vol. II, CPIA Publ. 308, 1979, pp. 35–50.
- <sup>101</sup>He, Y., Liu, X., Lin, M. C., and Melius, C. F., "Thermal Reaction of HNCN with  $\text{NO}_2$  at Moderate Temperatures," *International Journal of Chemical Kinetics*, Vol. 25, 1993, pp. 845–863.
- <sup>102</sup>Oyumi, Y., and Brill, T. B., "Thermal Decomposition of Energetic Materials 22. The Contrasting Effects of Pressure on the High-Rate Thermolysis of 34 Energetic Compounds," *Combustion and Flame*, Vol. 68, 1987, pp. 209–216.
- <sup>103</sup>Melius, C. F., "Theoretical Studies of the Chemical Reactions Involved in the Ignition of Nitramines," *Twenty-fourth JANNAF Combustion Meeting*, Vol. I, CPIA 476, 1987, pp. 359–366.
- <sup>104</sup>Edwards, G., "The Vapour Pressure of Cyclotrimethylene Trinitramine (Cyclonite) and Pentaerythritoltetranitrate," *Transactions of the Faraday Society*, Vol. 49, 1953, pp. 152–154.
- <sup>105</sup>Rosen, J. M., and Dickenson, C., "Vapor Pressures and Heats of Sublimation of Some High Melting Organic Explosives," *Journal of Chemistry and Engineering Data*, Vol. 14, 1969, pp. 120–124.
- <sup>106</sup>Taylor, J. W., and Crooks, R. J., "Vapour Pressure and Enthalpy of Sublimation of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX)," *Journal of the Chemical Society, Faraday Transactions I*, Vol. 72, 1976, pp. 723–729.
- <sup>107</sup>Cundall, R. B., Palmer, T. F., and Wood, C. E. C., "Vapour Pressure Measurements of Some Organic Explosives," *Journal of the Chemical Society, Faraday Transactions I*, Vol. 74, 1978, pp. 1339–1345.
- <sup>108</sup>Maksimov, Yu. Ya, Apal'kova, V. N., Braverman, O. V., and Solov'ev, A. I., "Kinetics of Thermal Decomposition of Cyclotrimethylenetrinitramine and Cyclotetramethylene-Tetranitramine in the Gas Phase," *Russian Journal of Physical Chemistry*, Vol. 59, 1985, pp. 201–204.
- <sup>109</sup>Kimura, J., and Kubota, N., "Thermal Decomposition Process of HMX," *Propellants and Explosives*, Vol. 5, 1980, pp. 1–8.
- <sup>110</sup>Beckstead, M. W., personal communication, Brigham Young Univ., Provo, UT, 1993.
- <sup>111</sup>Mitani, T., and Takahashi, M., "Temperature Measurements of Monopropellants Using a Counterflow Burner Method," *Western States Section of the Combustion Institute Spring Meeting*, 3C-050, 1988, pp. 161–163.
- <sup>112</sup>Lengellé, G., and Duterque, J., "Combustion de Propergols à Base d'Octogène," *Smokeless Propellant*, AGARD, CP-391, 1986, pp. 8-1–8-17.
- <sup>113</sup>Kubota, N., and Sakamoto, S., "Combustion Mechanism of HMX," *Nineteenth International Conference of the ICT*, 1988, pp. 65-1–65-12.
- <sup>114</sup>Parr, D. M., and Parr, T. P., "Condensed Phase Temperature Profiles in Deflagrating HMX," *Twentieth JANNAF Combustion Meeting*, Vol. I, CPIA Publ. 383, 1983, pp. 281–291.

<sup>115</sup>Liau, Y. C., and Yang, V., "Analysis of RDX Monopropellant Combustion with Two-Phase Subsurface Reaction," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 729–739.

<sup>116</sup>Maksimov, Yu. Ya., "Vapour Pressures of Aromatic Nitrocompounds at Various Temperatures," *Russian Journal of Physical Chemistry*, Vol. 42, 1988, pp. 1550–1552.

<sup>117</sup>Korsunskii, B. L., and Dubovitskii, F. I., "Kinetics of Thermal Decomposition of N,N'-Dimethylnitramine," *Doklady Akademii Nauk SSSR, (Soviet Physics—Doklady)*, Vol. 155, 1964, pp. 402–404.

<sup>118</sup>Lloyd, S. A., Umstead, M. E., and Lin, M. C., "Kinetics and Mechanism of Thermal Decomposition of Dimethylnitramine at Low Temperatures," *Journal of Energetic Materials*, Vol. 3, 1985, pp. 187–210.

<sup>119</sup>Shaw, R., and Walker, F. E., "Estimated Kinetics and Thermochemistry of Some Initial Unimolecular Reactions in the Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane in the Gas Phase," *Journal of Physical Chemistry*, Vol. 81, 1977, pp. 2572–2576.

<sup>120</sup>McMillen, D. F., Barber, J. R., Lewis, K. E., Trevor, P. L., and Golden, D. M., "Mechanisms of Nitramine Decomposition: Very Low Pressure Pyrolysis of HMX and Dimethylnitramine," Final Rept.,

SRI-Project PYU-5787, ARO, Menlo Park, CA, June 1979.

<sup>121</sup>Oxley, J. C., Hiskey, M., Naud, D., and Szekeres, R., "Thermal Decomposition of Nitramines: Dimethylnitramine, Diisopropylnitramine, and N-Nitropiperidine," *Journal of Physical Chemistry*, Vol. 96, 1992, pp. 2505–2509.

<sup>122</sup>Flournoy, J. M., "Thermal Decomposition of Gaseous Dimethylnitramine," *Journal of Chemical Physics*, Vol. 36, 1962, pp. 1106, 1107.

<sup>123</sup>Oyumi, Y., and Brill, T. B., "Thermal Decomposition of Energetic Materials 21. The Effect of Backbone Composition on the Products Evolved from Rapid Thermolysis of Linear Nitramines," *Combustion and Flame*, Vol. 67, 1987, pp. 121–126.

<sup>124</sup>Tobin, M. C., Fowler, J. P., Hoffman, H. A., and Sauer, C. W., "The Thermal Decomposition of Methylene Dinitramine," *Journal of the American Chemical Society*, Vol. 76, 1954, pp. 3249–3253.

<sup>125</sup>Robertson, A. J. B., "Thermal Decomposition of Explosives," *Transactions of the Faraday Society*, Vol. 44, 1948, pp. 677–682.

<sup>126</sup>Brill, T. B., and James, K. J., "Thermal Decomposition of Energetic Materials 62. Reconciliation of the Kinetics and Mechanisms of TNT on the Time Scale from Microseconds to Hours," *Journal of Physical Chemistry*, Vol. 97, 1993, pp. 8759–8763.