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Chemical Speciation and Dynamics in the Surface Combustion Zone of Energetic Materials

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An overview is presented of the status of chemical measurements of the condensed phase and the near-field gaseous phase of decomposing energetic materials. Various categories of energetic materials are surveyed first. The experimental and computational approaches for specifying the most important chemical reactions and rates in the condensed and near-surface gaseous phase are discussed along with the use of these chemical data in qualitative combustion models. Emphasis in the presentation is placed on the nitramines HMX and RDX.

I. Introduction

ONE of the most challenging problems in defining the details of the combustion of energetic materials and solid propellants has been the unavailability of the pathways and rates of the condensed-phase and near-field gas-phase reactions. The purpose of this paper is to present a current view of knowledge in this area. The types of energetic materials that are available are summarized to give an indication of the wide range of materials about which the condensed phase may need to be considered. Pyrolysis studies of the condensed phase are discussed from the point of view of both slow and fast heating rates. Approaches to learning the kinetics of the near-field gaseous radicals are presented. Finally, the incorporation of currently available chemical data into combustion models is overviewed.

II. Survey of Propellant Ingredients

The development of modern solid propellants can be linked to chemical advancements of the middle to late 19th century, in particular, nitration of hydroxyl groups to form nitrate esters such as nitroglycerin (NG) and nitrocellulose (NC). Double-base (DB) propellants derived from this process now include cast DB, extruded DB, composite-modified DB (CMDB), elastomer-modified CMDB (EMCMDB), and cross-linked DB propellants. The original DB formulations were produced by extrusion, which limited the diameter of grains to the presses available. During the 1940s, a gelation/slurry process was developed[1] that allowed casting of grains and thereby eliminated the massive presses needed to prepare high-density propellants. The CMDB formulations incorporate oxidizers and high-energy additives as a means of increasing propellant performance, whereas the EMCDB formulations incorporate an elastomer as a means of improving low-temperature physical properties of the propellant matrix.

Composite propellants incorporating a binder fuel, an oxidizer or monopropellant, and various additives were developed in the second half of the 20th century. The earliest such propellants were asphalt-based developed at the Guggenheim Aeronautical Laboratory, California Institute of Technology with oxidizers, such as potassium perchlorate and potassium nitrate. Polysulfide binders such as LP-33 were also employed to enable higher solids loading. More useful propellants, that is, higher performance and improved physical properties, evolved once polyester- and polyether-based polyurethanes became available for use in conjunction with oxidizers such as ammonium nitrate and, especially, ammonium perchlorate (AP). AP is still the most widely used oxidizer because of its availability, cost, and high oxygen content. Carboxyl-terminated materials, such as the copolymer of acrylic acid and butadiene (PBAA) and the copolymer of acrylonitrile and butadiene (PBAN), were developed next. These materials are still employed as needed, for example, in space shuttle boosters. The polybutadienes are the basis of most modern composite solid propellants with hydroxyl-terminated polybutadiene (HTPB) currently being the most widely used because of its low viscosity and attendant capability of producing propellants with high solids loading and excellent physical properties. Davenas[2] and Singh[3] discuss these classes of solid propellants, as well as many of the topics that follow.

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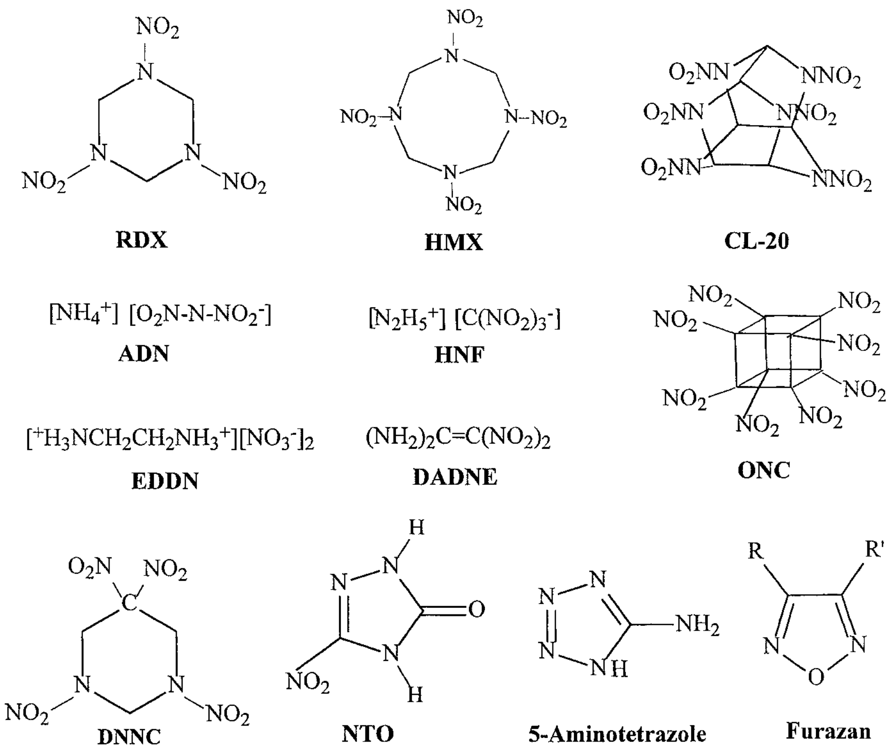


Fig. 1 Structures of selected compounds.

Metallic fuels are frequently added to increase the specific impulse I_{sp}. Aluminum powder is the focus primarily because it yields the second highest volumetric heat release through Al_2O_3 formation. Only beryllium and the attendant formation of BeO rank higher,[4] but beryllium propellants are generally impractical because of the extreme toxicity of the combustion products and the reduced density. Although boron appears to be an attractive candidate energetically, its oxidation does not yield B_2O_3 alone because of the equilibrium with gaseous HBO_2 and an attendant decrease in heat release. Zirconium, which yields ZrO_2, may be employed in propellants that require higher overall density because zirconium powder is nearly 2.5 times more dense than Al powder. The high density overcomes somewhat the lower energy released by the production of ZrO_2 relative to Al_2O_3. Magnesium has been considered as a partial replacement for Al because of environmental factors to be mentioned. In addition, it is relatively easy to achieve complete combustion of Mg. Metal hydrides such as AlH_3, BeH_2, and ZrH_2 appear to be promising fuels because of their high heat release, but virtually all metal hydrides are incompatible with the polymers and/or the curing agents employed in present-day binders. Their application to propellants is severely limited without further developments in coating technology.

The space shuttle program has raised environmental questions about the use of AP-based propellants. Discussion of these issues is available.[5] Elimination of HCl as a product is a major environmental objective. If needed, this goal might eventually be achieved by the use of alternate primary oxidizers[6] or by chemically binding the HCl by a 1:1 molar substitution of AP by sodium nitrate to form NaCl on combustion. Another method under consideration is to bind HCl as $MgCl_2$ through the partial substitution of Al by Mg.

Finally, small amounts of additives are sometimes incorporated to influence a specific ballistic effect. For instance, catalysts may accelerate (or sometimes suppress) the overall combustion rate of the base propellant. In addition, catalysts often reduce the sensitivity of combustion rate to changes in the combustion pressure or propellant temperature. These catalysts or suppressants can be solids, such as fine Fe_2O_3, or liquids, such as *n*-butyl ferrocene and selected carboranes. Atwood et al.[7] overviewed the characteristics of the most widely utilized catalysts on the combustion of solid oxidizers. Another important use of additives is to eliminate combustion instability, which is characterized by high-amplitude oscillations in the chamber pressure. It has been demonstrated[8] that incorporation of a small amount of appropriately sized Al particles can suppress such instability.

Most of the currently utilized solid propellants are based on C–H–O–N materials or the perchlorate ion and Al, as already mentioned. The theoretical I_{sp} of these propellants, along with certain propellants that contain fluorine, is discussed by Lempert et al.[9,10] Advanced solid propellant ingredients incorporate new oxidizers and/or use new binder/plasticizers. Some of these are shown in Fig. 1. Both DB and composite propellants currently in use sometimes incorporate the two well-known cyclic nitramines, RDX and HMX. Their primary value is to optimize oxygen balance, while increasing the heat of formation, thereby maximizing the formulation I_{sp}. In the past decade, hexanitrohexazaisowurtzitane (HNIW), a cage nitramine, has attracted much attention.[11,12] In addition to an improved oxygen balance, HNIW possesses a higher density (2.02 g/cm^3) than HMX (1.908 g/cm^3) and a higher energy content based on the heat of formation. The oxidizer attracting the second most attention as a new propellant ingredient is ammonium dinitramide (ADN). ADN was first described by Pak.[13] Luk'yanov and Tartakovsky[14] surveyed the synthesis of dinitramide salts. However, the utility and long-term viability of ADN is debatable because of questions regarding control of the burning rate and impact sensitivity of propellants containing significant amounts of ADN. Hydrazinium nitroformate (HNF) (Ref. 15) has been a candidate oxidizer for 40 years.[16] Considerable progress has been made recently largely by producing desirable crystal properties that reduce the sensitivity to impact and friction. It is still too early, however, to declare HNF a viable propellant ingredient. The high sensitivity of burning rate to pressure[17] remains an issue. The synthesis of octanitrocubane (ONC) was achieved by Zhang et al.[18] The density (1.99 g/cm^3) is lower than predicted, and additional work is required to determine if the energy released matches theoretical predictions.[19]

The largest volume of research on high-energy ingredients has recently centered on high-nitrogen heterocyclics, such as triazoles, tetrazoles, and furazans, some of which are discussed in the next section. The liquid and solid furazans have attracted the greatest attention. These compounds demonstrate a relation of burning rate to molecular structure that could be quite useful.[20–22] Sheremetev[23] and Tselinskii et al.[24] have summarized these areas. Another new oxidizer, diaminodintroethylene (DADNE or FOX-7), has potential.[25] The incorporation of the difluoroamino ($—NF_2$) group, a focus of extensive research in the 1960s,[26] has resurfaced in syntheses of cyclic[27] and linear[28] nitramines. Possible combinations of $—NF_2$ with other energetic moities have been reported.[29]

Many families of new advanced oxidizers are represented by the structure, $R[CH_2X]_2$, where X can be 1) $-C(NO_2)_3$, 2) $-C(NO_2)_2NF_2$, 3) $-C(NO_2)_2CH_2N_3$, 4) $-C(NO_2)_2N_3$, 5) $-C(NO_2)_2C(NO_2)_3$, and 6) $-C(NO_2)_2F$. The literature is rich with information on these compounds, but the most recent work is on types 3 and 4 (Refs. 30–32). The pentanitro-terminated materials 5) have been described.[33] Agrawal[34] recently surveyed this area.

A considerable effort has been devoted for two decades to develop new energetic polymers. Glycidyl azide polymer (GAP)[35] has been most thoroughly investigated as a result of its acceptable density (1.3 gm/cm^3), positive heat of formation, and unique ability to desensitize NG (Refs. 36–38). GAP has been employed both as a binder and as an energetic plasticizer. Many other promising energetic polymers are now reaching scaleup status and D'Andrea et al.[39] have broadly described several. The two main categories of polymers are 1) $H-[O-CH_2-CR_1R_2-CH_2]_x-OH$ {oxetanes}, where $R_1 = R_2 = CH_2N_3$ {BAMO}, $R_1 = CH_3$, $R_2 = CH_2N_3$ {AMMO}, and $R_1 = CH_2ONO_2$, $R_2 = CH_3$ {NMMO} and 2) $H-[O-CR_1R_2-CH_2]_x-OH$, where $R_1 = H$, $R_2 = CH_2N_3$ {GAP}, $R_1 = H$, $R_2 = CH_2ONO_2$ {PGLYN or PGN}, and $R_1 = CN$, $R_2 = NF_2$ {PCDE}. The status of category 2 was recently given.[40] Two additional $—NF_2$ polymers of note are category 1 (Ref. 41), where $R_1 = R_2 = CH_2NF_2$ and 2, where $R_1 = H$ and $R_2 = CH_2-O-CH_2-CH_2-CH_2-C(NF_2)_2-CH_3$ (Ref. 42). Polymers that contain substantial fluorine facilitate the use of boron because BOF will be formed instead of the mixture of B_2O_3 and HBO_2 mentioned earlier. Additionally, reduction in two-phase flow losses in the nozzle that result from the formation of gaseous AlF, rather than solid Al_2O_3, yields a higher overall I_{sp}.

Given the wide variety of energetic materials, additives, and formulations that are possibly useful, it is likely that, however desirable, large test matrices will not be available. Thus, new opportunities to advance the field of rocket propulsion increasingly will rest on predictive capability. For instance, understanding the relation between the decomposition of energetic materials and their combustion characteristics is a central objective.[43] The tendency to form particular species in suitable amounts in the surface reaction zone is required knowledge to model combustion and combustion stability. Thus, detailed studies of the condensed-phase kinetics and mechanisms, which are discussed next, form a molecular foundation for the initiating processes. Given the wide variety of materials discussed, we limited the following sections primarily to illustrations with the nitramines RDX and HMX, for which considerable advances have been made in recent years.

III. Decomposition of Energetic Materials and Formulations

A. Low Heating Rates

The decomposition chemistry of energetic materials and their formulations is of course an essential component of the combustion process. Experiments carried out on nitramines at slow heating rates provide information at a moderate level of detail. For example, it is possible to make global reaction rate measurements because the temperature of the sample is well known. Also, it is possible to use species-selective detection methods so that reaction rates for specific product channels can be measured independently. These types of studies are well suited for determining reaction rates in hazards situations, such as under slow cookoff conditions. This accident scenario represents the highest danger of violent reaction, including the possibility of a deflagration-to-detonation transition as the reaction wave propagates through thermally damaged material. A disadvantage of the slow heating techniques is that the reaction mechanisms may be different for slow and fast heating events (discussed later), so that reaction kinetics determined under slow heating conditions might not be useful to predict the rates of fast reactions that occur under combustion conditions.

Numerous authors have investigated the rates and mechanisms of decomposition of RDX and HMX under slow heating conditions.[44–48] Of particular note is the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) technique. This instrument allows the rate of selected gas-phase product formation to be measured as a function of time. Detailed descriptions of the apparatus and data collection procedures have been described by Behrens.[49–51] The results of the STMBMS analysis show that RDX and HMX have similar decomposition mechanisms, as well as similar degradation products.[49,50,52–57] The common degradation products for both RDX and HMX observed via STMBMS are N_2O, CH_2O, NO, H_2O, and CH_3NHCHO. Behrens and Bulusu[53,55] and Behrens[56] have also carried out experiments on isotopically labeled materials to gain additional mechanistic information about the reaction products that arise from labeled functional groups in the starting material.

Evidence suggests that the first observable gaseous product is N_2O. Detecting the degradation products during decomposition is vital because it allows one to determine the specific bonds that are breaking, as well as the order in which they break. From these data, one can make kinetic assignments to specific bonds, which aids in determining the overall degradation mechanism. Using model-fitting techniques, for example, Behrens and Bulusu[58] calculated an activation energy of 48 kcal mol^{-1} for the initial decomposition region in HMX. The N–N bond is the weakest in the molecule with an energy of 47.5 kcal mol^{-1}.

One of the challenges of studying reaction kinetics of solid materials is that the reaction rate laws frequently do not obey simple order-n kinetic expressions. This is because, unlike the gas phase, elementary steps of the reaction sequence do not take place in isolated unimolecular reactions or binary collisions. Moreover, the reaction environment may be altered dramatically at the ending stages of reaction compared with the starting material. To address this issue, model-free kinetic methods have been developed to describe rates of reactions without making assumptions about the functional form of the reaction model. Thus far, the applications of these kinetic analysis methods have been applied to globally measured reaction rates, such as measurements of gas formation rate by thermogravimetric analysis or heat production by differential scanning calorimetry. One of the big advantages of the model-free methods of kinetic analysis is that they can be used to determine the kinetics of composite explosives and propellants, which are usually mixtures of oxidizers, fuels, polymeric binders, plasticizers, and cross-linking agents. These chemically complex mixtures can exhibit several successive stages of reaction that may overlap one another and, therefore, be difficult to analyze using traditional model-fitting methods.

One specific propellant sample that was studied by Peterson and Wight[59] consisted of 83% HMX and 17% binder of which HTPB was a major component [binder composition: R-45M (HTPB): 7.52%, dioctyladipate (DOA): 8.12%, lecithin: 0.7%, isophorone diisocyanate (IPDI): 0.62%, and triphenyl bismuth (TPB): 0.04%]. This analysis showed that the propellant degraded in a three-step process. The first step was attributed primarily to the binder material. The second step was the HMX degradation, and the third step was due to the HTPB binder additive. It was also noted that the addition of these specific binder materials caused some of the HMX to degrade at a lower than normal temperature.

Kinetic analyses have been conducted on the propellant using a model-free isoconversional method that allows the activation energies as a function of degradation to be determined.[60–62] This method is particularly useful in that it tracks the activation energy changes during the entire decomposition process and ultimately allows a more kinetically accurate assignment of the degradation steps and processes. For the HMX–binder mixture mentioned, the results showed a nearly constant energy value of 6 kcal mol^{-1} for the first degradation step. The HMX stage had an average value of 29 kcal mol^{-1}, whereas the final HTPB step showed values near

60 kcal mol^{-1}. These HTPB energies were compared to those of pure HTPB and agreed well.

The slow heating methods can provide a high degree of detailed information about both the mechanisms and rates of reaction of chemically complex composite propellants and explosives. The results can be used to make predictions of accident scenarios that involve slow heating, and in some cases may also be extrapolated to high temperature to predict combustion behavior. There is, however, no true substitute for high heating rate data if combustion modeling is the objective.

B. High Heating Rates

The combustionlike pyrolysis of energetic materials liberates products that initiate the flame zone. High-rate pyrolysis studies, which emphasize the condensed phase, can be grouped according to the method of heating: infrared laser and hot surface. A number of variations of these two methods have been developed and so the focus here will be on the methods used in the past 10 years that are aimed at understanding the mechanisms and kinetics of energetic materials.

1. CO_2 Laser Heating

The CO_2 laser can be used in the pulsed or continuous wave mode to decompose the surface layer at heating rates on the order of 10^7°C/s. Two advantages of this method are that very fast heating can be achieved and chemical diagnostic techniques can be used in conjunction to determine the products that are formed. A disadvantage is that independent specification of the heating rate and final temperature is not achieved so that kinetic determinations are difficult or impossible.

Botcher and Wight[63,64] employed a single laser pulse to heat a film of RDX sandwiched between two transparent windows at liquid nitrogen temperature. By the use of Fourier transform infrared (FTIR) spectroscopy, this work demonstrated that cleavage of the N–NO_2 bond is the initial step in fast decomposition of RDX. The same method has been applied to determine the products of GAP and Polyglycidyl nitrate (PGN) (Ref. 65). Studies of the decomposition products of RDX and HMX during rapid heating by a CO_2 laser have also been conducted by Lee et al.,[66] Litzinger et al.,[67] and Tang et al.[68] Laser fluxes of 50–400 W/cm^2 were used during these experiments, which were primarily conducted at atmospheric pressure in argon. Quartz microprobes were used to extract samples of gas-phase products near the sample surface, and Tandem mass Spectrometry (MS/MS) with collision-induced dissociation (CID) was applied to identify and quantify the products. The most probable chemical structures for the products were deduced from the observed CID/MS, available results in the literature, and calibration to confirm the identification, when standards could be obtained. Surface temperatures were measured using microthermocouples of the W/Re and Pt/Rh type with 5–25 μm diameter.

Advantages of probe sampling and analysis by mass spectrometry are that, in principle, all stable gas-phase species including N_2 and H_2 can be quantified and that mass closure can be attempted. The experimental approach based on physical sampling has the disadvantage that the probe may perturb the chemistry or that reactions can occur in the probe. Keeping the probe tip as small as possible and using quartz minimize perturbation of the reactions. The effects of reactions in the probe have been investigated with modeling and found to have only a small effect on even the most reactive species such as NO_2 and H_2CO.

Major stable species observed near the sample surface were similar to those observed by other researchers. For RDX and HMX, the major products were NO_2, N_2O, NO, CH_2O, CO, N_2, HCN, and H_2O. No CO_2 was observed at the sample surface. The mole fraction of N_2 at the sample surface was approximately 0.05 for both RDX and HMX regardless of the incident heat flux. At a heat flux of 100 W/cm^2, HMX was found to have higher levels of H_2CO and NO_2 near the surface than RDX. At 300 W/cm^2, the levels of NO_2 for RDX rose to levels comparable to those for HMX, but the difference in H_2CO remained. Surface temperatures measured were approximately 340°C for RDX and approximately 380°C for HMX, similar to those reported by other researchers. No significant variation of surface temperature with laser heat flux was observed, and so it was not possible to determine the effect of surface temperature on species composition or to estimate branching ratios between the two major paths of nitramine decomposition postulated by Brill[69] and discussed subsequently.

The RDX results showed H_2CNH, which was not previously reported. This species was detected in the CID spectrum by the signal at 29 m/z based on a strong peak at 14 m/z, which could not be accounted for by the HCO ionization fragment of H_2CO. HCO is the other species contributing to the signal at m/z of 29. Based on a calculated sensitivity factor, the mole fraction of H_2CNH at the RDX surface was estimated to be 0.01. H_2CNH was not observed in the HMX results, which is probably because very little of the HMX decomposes in the gas phase compared to RDX at the conditions tested.

Other products with low mass fractions were observed at m/z ratios of 43, 45, 47, 54, 70, 81, and 97 for both RDX and HMX. Multiple CID experiments with different levels of collision energy were performed to determine the likely structures of these products. Among the largest of these products was the signal at m/z of 81, which was identified as triazine based on its CID spectrum. The identification was confirmed by obtaining mass spectra from triazine. Zhao et al.[70] previously reported triazine as a product of the gas-phase decomposition of RDX, but the CID spectrum was the first reported measurement of triazine as a product of decomposition for HMX. Previously, Behrens[56] reported triazine as a product of electron impact ionization of HMX in a study of solid phase decomposition. However, in this work, none of the other products reported by Behrens to be formed during electron impact ionization of HMX were observed, so that the triazine is believed to be an actual decomposition product of HMX. Calibration using triazine showed that the near-surface mole fraction was about 0.025 for both RDX and HMX. The signal at m/z of 54 was found to be due to the fragmentation of triazine during ionization.

Although the signal at m/z of 97 was small for both RDX and HMX, CID analysis of its structure was attempted because Behrens and Bulusu also reported this species.[58] For HMX, CID analysis was possible, and the spectrum was consistent with that of oxy–s–triazine. The species at 70 m/z was found to have the chemical composition of $C_2N_2H_2O$, consistent with the work of Behrens and Bulusu.[58] Based on the CID spectrum of this species, its structure is consistent with that proposed by Goshgarian.[71]

The CID spectrum of the species at 47 m/z showed a major peak at 30 m/z, and a very small peak at 17 m/z. Because HONO is expected to give these two peaks, HONO is assigned to this species. Based on the CID spectrum of the species at 45 m/z, formamide is the most plausible candidate for the species. Behrens[56] also observed the species at mass 45 as a fragment of N–methylformamide due to ionization, and Behrens and Bulusu[58] found formamide during the solid-phase decomposition of HMX. The CID spectrum for the species at 43 m/z showed eight peaks and no major distinctive patterns. However, the spectrum was consistent with HNCO as the composition of the species at this m/z.

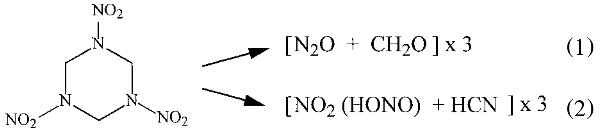
In general MS methods of detection are the most powerful techniques to identify species in the gaseous phase. The chemical structures can frequently be deduced from CID MS/MS methods, although the bond connectivity is not absolutely revealed. This leaves open the door for other approaches to complement mass analysis.

2. Hot-Filament Heating

Hot-surface or filament heating methods offer the advantages of fast pyrolysis with independent control over the heating rate and final temperature. The sacrifice is that the heating rates are lower than are possible with the CO_2 laser. To date, the most widely applied method of this type is temperature-jump (T-jump)/FTIR spectroscopy, which employs an electrically heated platinum filament.[72] The analogous technique with Raman spectroscopy has recently been reported, thus enabling mass closure to be achieved.[73] Modeling of the platinium filament, sample, and surroundings as a system reveals that heating rates up to 600°C/s are achievable while stopping and holding at a known and adjustable temperature.[74,75] The control voltage of the filament can be recorded simultaneously with rapid-scan FTIR spectra of the evolved products to obtain thermochemical information, product sequencing, and formation rates. Catalytic effects of the filament have been shown to be negligible.[76] Kim and Thynell[77] devised a variation on this method in which a heated cavity is employed in place of the filament. This approach improves the heat transfer to the sample but sacrifices on the opportunity to detect the earliest quenched products.

T-jump/FTIR spectroscopy has provided mechanistic information, for example, on HMX and RDX (Ref. 69), AP (Ref. 76), ADN (Ref. 78), DNNC (Ref. 79), EDDN (Ref. 80), HNF (Ref. 81), metal salts of NTO (Ref. 82), aminotetrazoles,[22] and substituted furazans.[83] It has been applied to obtain kinetic information on HMX and RDX (Ref. 84), poly (styrene peroxide),[85] HTPB (Ref. 86), polyethyleneglycol,[87] cellulose acetate butyrate (CAB),[88] and GAP (Ref. 89). Mixtures of energetic materials are among the more difficult systems to study, but results have been obtained on AP/HTPB (Ref. 90), RDX/CAB (Ref. 91), and RDX/GAP (Ref. 92). The products are quantified by multivariate analysis[93] enabling complex mixtures of products to be resolved. Good elemental atom balances can be obtained by combining the infrared (IR) and Raman methods, which provide complementary information.[73]

More detailed mechanistic insight has been gained on RDX and HMX by the use of T-jump/FTIR spectroscopy[75,69,88,94] than has been possible with CO_2 laser heating. The decomposition channels for at flash heating conditions appear to be represented by the global reactions (1) and (2),



which together are experimentally found to be approximately thermally neutral.[69] Reaction (1) is favored at lower temperatures, whereas Reaction (2) dominates at higher temperatures. Consistent with lower heating rate results,[52,54] the nitrogen oxides are liberated before the other products.

The Arrhenius parameters for reactions (1) and (2) have been extracted from these experimental data[84] and used in combustion models in which pathway chemistry has been incorporated. The rationale is given in more detail in Sec. V. Heat was proposed to be generated in bubbles by reaction (3) with a heat of reaction of about -44 kcal mol^{-1}:

$$CH_2O + NO_2 \rightarrow NO + CO + H_2O \qquad (3)$$

In addition to the major products from RDX (NO_2, NO, N_2O, CO, CO_2, CH_2O, HCN, H_2O, etc.) also observed by CO_2 laser heating and mass spectrometry, the approximate identity and temperature dependence of volatile minor products (defined as $<4\%$ mole fraction) from thermal decomposition RDX have been determined by multivariate regression of the IR spectra in the 265–325°C range.[95] The gaseous phase products include HNCO, HONO, hexahydro-1-nitroso-3, 5-dinitro-*s*-triazine, *s*-triazine, amides modeled as C-hydroxyl-N-methylformamide, and both RDX vapor and RDX aerosol. The CO_2 laser and filament heating work described here, previous studies of slower decomposition of RDX,[49,52–57] and studies on quenched burning samples of RDX-containing propellants[94,96] enable the description of products from RDX decomposition to be unified over a wide range of heating and temperature conditions.

The identity of the species liberated by slow and fast decomposition of the condensed phase along with details, such as the temperature and pressure dependencies of their concentrations and rates of liberation to the primary reaction zone of the flame, are essential for modeling of steady and transient combustion. The field of condensed-phase decomposition kinetics and mechanisms is, however, far from a satisfactory state in terms of the necessary details. The phase heterogeneity, spatially small reaction zone, and temperature and concentration gradients complicate the acquisition of detailed information. By contrast, the gas-phase chemistry is more tractably investigated, both experimentally and computationally.

IV. Kinetics of Near-Field Exothermic Reactions

Pyrolysis and evaporation lead to liberation of gaseous products from the propellant surface. The reactions involving these large- and mid-size free radicals and molecules dominate the early stages of propellant flame zone. Of particular interest are the exothermic reactions because these provide heat at the surface, affect the burning rate, and couple instabilities in the gaseous phase to the burning surface. The rates of some of these reactions can be determined experimentally. For example, a laser provides an intense tunable light source between 200 and 800 nm applicable for millisecond to nanosecond chemical kinetic methods including discharge flow,[97] high-temperature fast flow,[98] and dual-flash pump probe.[99] The various methods for generation and detection of reactive intermediates in the gas phase are described by Setser.[100] The availability of the broadly tunable cw ring dye laser and broad-beam, rare-gas excimer lasers has reinvigorated the shock tube as the most effective high-temperature reactor. Various free radicals can be selectively generated by pulsed photolysis behind incident or reflected shock waves at practically any temperatures above 500°C using diagnostic methods, such as atomic resonance and resonant laser absorption,[101] laser-induced fluorescence, and, potentially, the ultrasensitive cavity ringdown absorption technique.[102]

Unfortunately, most of the radicals from nitramines, such as $HNNO_x$ and CH_2NNO_x ($x = 1$, 2,), do not fluoresce from their excited states (which are also unknown experimentally and theoretically). Accordingly, they cannot be readily detected by optical diagnostics under combustion conditions. In addition, these reactive intermediates are difficult to prepare neatly in the laboratory for kinetic studies. Theoretical prediction of their thermal energetics and decomposition mechanisms becomes the only means to obtain their kinetic parameters over a wide range of temperature and pressure as needed for computer simulation of burning and stability characteristics.

Advances have been made recently in the calculation of the potential energy surfaces of reactant radicals using the modified Gaussian-2 (G2M) computational method (see Ref. 103). The method employs a series of calculations to improve electron correlation and the expansion of basis sets using the geometry optimized with a hybrid density function theory [typically the Becke-style 3-parameter using Lee-Yang-Parr correlation functions (B3LYP) method with the 6-311G(d, p) Gaussian basis set]. The predicted G2M energies for systems containing as many as eight heavy atoms approximate the values one would obtain at the Coupled cluster with singles, doubles and triples CCSD(T)/6-311 + (3df, 2p) level of theory.[103] The G2M method predicts the heats of atomization for the 32 first and second row compounds employed in the original G2 method by Curtiss et al.[104] with about 1 kcal/mol absolute deviation from experimental values.

The major reaction paths for all radical–radical reactions take place in the near field via long-lived intermediates, usually without well-defined transition states. Accordingly, the computationally simple transition-state theory (TST),[105] which is quite useful in predicting direct metathetical (or exchange) reaction rates, is no longer applicable in this case. To circumvent the difficulty, the “transition state” for a barrierless radical–radical reaction can be defined canonically for each temperature at the separation in which the maximum Gibbs free energy of the association complex is predicted with a full quantum mechanical calculation of the geometry and vibrational frequencies. These molecular parameters including energy, 3N-7 (or 3N-6 for a linear complex) vibrational frequencies and moments of inertia, are then employed for multichannel statistical theory [such as Rice–Ramsperger–Kassel–Marcus (RRKM)] (see Ref. 105). calculations to predict rate constants for all individual product channels. Detailed descriptions of this approach are available.[106–110]

Elementary processes relevant to RDX, HMX and ADN decomposition reactions near their burning surfaces are briefly summarized in the two following subsections, one for the unimolecular decomposition reactions and related reverse radical association reactions

Table 1 Rate constants predicted for unimolecular and related reverse reactions[a]

Reaction	T, K	P, atm	k
$HN(NO_2)_2 \rightarrow HNNO + NO_2$	300–1000	200	$6.9 \times 10^{16}\ \exp(-18{,}300/T)$
$HNNO_2 \rightarrow NH + NO_2$	500–2000	200	$7.3 \times 10^{44}\ T^{-9.3}\ \exp(-24{,}100/T)$
$CN_2NNO_2 \rightarrow CH_2N + NO_2$	500–1500	200	$7.3 \times 10^{57}\ T^{-11.0}\ \exp(-26{,}100/T)$
$\rightarrow HCN + HONO$	——	——	$1.5 \times 10^{11}\ \exp(-14{,}200/T)$
$\rightarrow CH_2O + N_2O$	——	——	$2.9 \times 10^{9}\ \exp(-16{,}400/T)$
$CH_2NO \rightarrow HCN + OH$	200–2000	200	$1.8 \times 10^{10}\ \exp(-25{,}600/T)$
$CH_2N \rightarrow HCN + H$	500–2000	200	$1.5 \times 10^{12}\ \exp(-14{,}000/T)$
$CH_2N + M \rightarrow HCN + H + M$	500–2000	0^{b}	$3.8 \times 10^{11}\ T^{1.0}\ \exp(-10{,}800/T)$
$NH + NO \rightarrow H + N_2O$	300–3000	200	$7.1 \times 10^{9}\ T^{0.83}\ \exp(1{,}100/T)$
$\rightarrow OH + N_2$	——	——	$1.8 \times 10^{9}\ T^{0.83}\ \exp(1{,}100/T)$
$NH + NO_2 \rightarrow HNNO_2$	300–3000	∞^{c}	$1.4 \times 10^{16}\ T^{-0.73}\ \exp(-617/T)$
	——	0	0
$\rightarrow N_2O + OH$	300–3000	0	$2.1 \times 10^{13}\ T^{-0.49}\ \exp(360/T)$
	——	∞^{c}	0
$NH + NO_2 \rightarrow HNO + NO$	300–3000	<200	$1.3 \times 10^{6}\ T^{2.0}\ \exp(1{,}180/T)$
$CH_2N + NO \rightarrow CH_2NNO$	300–3000	200	$1.1 \times 10^{38}\ T^{-8.1}\ \exp(-330/T)$
$\rightarrow HCN + HNO$	——	——	$4.2 \times 10^{2}\ T^{2.7}\ \exp(-3{,}400/T)$
$CH_2N + NO_2 \rightarrow CH_2NNO_2$	500–1500	200	$1.0 \times 10^{33}\ T^{-6.5}\ \exp(-2{,}800/T)$
$\rightarrow HCN + HONO$	——	——	$3.6 \times 10^{6}\ T^{1.4}\ exp(-1{,}050/T)$
$\rightarrow CH_2O + N_2O$	——	——	$1.5 \times 10^{4}\ T^{1.7}\ \exp(-3{,}700/T)$
$CH_2N + OH \rightarrow H_2CNOH$	300–3000	200	$2.4 \times 10^{22}\ T^{-2.9}\ \exp(-2{,}100/T)$
$\rightarrow HCN + H_2O$	——	——	$1.7 \times 10^{19}\ T^{1.8}\ \exp(-1{,}500/T)$
$NCO + NO \rightarrow N_2O + CO$	300–3000	<200	$4.0 \times 10^{19}\ T^{-2.2}\ \exp(-877/T)^{d}$
$\rightarrow N_2 + CO_2$	——	<200	$1.5 \times 10^{21}\ T^{-2.7}\ \exp(-918/T)^{d}$

[a] The original publications can be found in Ref. 112. Unimolecular rate constants at the pressure indicated are given in s^{-1} and bimolecular and second-order decomposition in cm^3/mol-s.

[b] Low-pressure limit.

[c] High-pressure limit.

[d] Ref. 113.

and the other for bimolecular processes not directly related to unimolecular reaction systems.

A. Unimolecular Reactions

Unimolecular and related reverse reactions illustrated by reactions (4–6) commonly take place in high-temperature combustion reactions:

$$AB \underset{+M}{\overset{+M}{\rightleftarrows}} AB^{\surd} \rightarrow A + B \quad \text{(unimolecular decomposition)} \tag{4}$$

$$\begin{aligned} A + B \rightleftarrows AB^{\surd} &\rightarrow AB(+M) \quad \text{(association/stabilization)} \\ &\rightarrow C + D \quad \text{(association/decomposition)} \end{aligned} \tag{5}$$

or

$$\begin{aligned} A + B \rightleftarrows BA^{\surd} &\rightarrow BA(+M) \\ &\rightarrow E + F \end{aligned} \tag{6}$$

where $\surd$ represents internal excitation resulting from collisional activation ($AB + M$) or chemical activation ($A + B$). AB and BA are two structural isomers. A specific example of processes (4–6) is given with reactions (7–9) for the decomposition of the first radical intermediate produced by the decomposition of dinitramidic acid, $HN(NO_2)_2$. These reactions are pivotal to the initiation of the ADN combustion reaction:

$$HNNO_2 \underset{+M}{\overset{+M}{\rightleftarrows}} HNNO_2^{\surd} \rightarrow NH + NO_2 \tag{7}$$

$$\begin{aligned} HN + NO_2 \rightleftarrows HNNO_2^{\surd} &\rightarrow HNNO_2(+M) \\ &\rightarrow NN(O)OH^{\surd} \rightarrow N_2O + OH \end{aligned} \tag{8}$$

$$\begin{aligned} NH + NO_2 \rightleftarrows HNONO^{\surd} &\rightarrow HNONO(+M) \\ &\rightarrow HNO + NO \end{aligned} \tag{9}$$

The rate constants calculated with canonical variational RRKM theory for the unimolecular decomposition of $HN(NO_2)_2$ and $HNNO_2$ and the bimolecular $NH + NO_2$ reactions just given are listed in Table 1. These rate constants have been employed for kinetic modeling of ADN decomposition (Fig. 2) under low-pressure conditions.[111] Similar calculations have been performed for the unimolecular decomposition of CH_2NNO_x ($x = 1, 2$) and related bimolecular reactions, $CH_2N + NO_x$, as well as the $CH_2N + OH$ reaction, which are part of the nitramine scheme. The results of these calculations are also summarized in Table 1 (see Refs. 112 and 113).

B. Bimolecular Reactions

Many bimolecular reactions involving HNO, HONO, and HNO_3 are key reactive intermediates in nitramine and AP combustion reactions. Many of these reactions not only take place by the simple metathetical, that is, direct exchange, mechanism but also by multiple indirect complex-forming mechanisms. For example, the reaction of H with HONO was found to occur primarily by indirect addition/decomposition processes (10) and (11),[110] instead of the commonly assumed direct abstraction process (12):

$$H + HONO \rightleftarrows HON(O)H^{\surd} \rightarrow HNO + OH \quad \text{(addition/decomposition)} \tag{10}$$

$$H + HONO \rightleftarrows N(OH)_2^{\surd} \rightarrow NO + H_2O \quad \text{(addition/decomposition)} \tag{11}$$

$$H + HONO \rightarrow H_2 + NO_2 \quad \text{(direct abstraction)} \tag{12}$$

In this mechanism, both cisisomers and transisomers of HONO are involved, but the cisisomer generally provides lower energy paths to the products listed. Similar complex mechanisms were found to hold for several other reactions: $HNO + NO_2$ (Ref. 114), $OH + HONO$ (Ref. 115), $OH + HNO_3$ (Ref. 116), $HONO + HONO$ (Ref. 117), and $HONO + HCl$ (Ref. 118), among others. The results for these and other reactions computed with TST (for direct reactions) and RRKM (for complex-forming reactions) are summarized in Table 2 (see Refs. 110, 112, 115, 118, and 119) for kinetic modeling in combustion applications. Currently the National Institute of Standards and Technology kinetics database is an important source of other elementary reaction rate constants.[120] (The most recent version can be directly accessed at http: //kinetics.nist.gov/index.php.)

This section is only a brief introduction to the power of computational methods to sort out near-surface gas-phase flame reactions of energetic materials that are difficult or impossible to measure. Obviously the subject is complex, and the number of flame reactions is large. As this field expands, however, the calculated rate constants

Table 2 Rate constants predicted for biomolecular reactions[a]

Reaction	T, K	k (cm^3/mole · s)	Reference
$NO + HN_3 \rightarrow HNO + NH_2$	300–5000	$1.0 \times 10^7 T^{1.7}$ exp($-28{,}500/T$)	a
$NO_2 + NH_3 \rightarrow HONO + NH_2$	300–5000	$1.2 \times 10^1 T^{3.4}$ exp($-11{,}300/T$)	a
$HNO + NO_2 \rightarrow HONO + NO$	300–5000	$4.4 \times 10^1 T^{2.6}$ exp($-2{,}034/T$)	a
$H + HONO \rightarrow H_2 + NO_2$	300–3500	$2.0 \times 10^8 T^{1.6}$ exp($-3{,}300/T$)	110
$\rightarrow OH + HNO$	——	$5.6 \times 10^{10} T^{0.86}$ exp($-2{,}500/T$)	110
$\rightarrow H_2O + NO$	——	$8.1 \times 10^6 T^{1.9}$ exp($-1{,}900/T$)	110
$OH + HONO \rightarrow H_2O + NO_2$	200–500	$4.1 \times 10^{12} (T/300)^{-0.8}$	115
	500–2000	$1.8 \times 10^7 T^{1.5}$ exp($1{,}260/T$)	a
$H + HNO_3 \rightarrow H_2 + NO_3$	300–3000	$5.6 \times 10^8 T^{1.5}$ exp($-8{,}200/T$)	a
$\rightarrow OH + HONO$	——	$3.8 \times 10^5 T^{2.3}$ exp($-3{,}500/T$)	a
$\rightarrow H_2O + NO_2$	——	$6.1 \times 10^1 T^{3.3}$ exp($-3{,}200/T$)	a
$OH + HNO_3 \rightarrow H_2O + NO_3$	750–1500	$8.7 \times 10^1 T^{3.5}$ exp($839/T$)	116
$HNO + HONO \rightarrow H_2O + 2NO$	300–3000	$1.7 \times 10^{-3} T^{4.2}$ exp($-8{,}350/T$)	119
$HONO + HCl \rightarrow H_2O + ClNO$	300–3000	$1.1 \times 10^2 T^{3.0}$ exp($-5{,}120/T$)	118
$HONO + NO_2 \rightarrow HNO_3 + NO$	300–5000	$2.0 \times 10^2 T^{3.3}$ exp($-15{,}400/T$)	118
$HONO + HONO \rightarrow NO + NO_2 + H_2O$	300–5000	$3.5 \times 10^{-1} T^{3.6}$ exp($-6{,}100/T$)	a
$HONO + NH_3 \rightarrow H_2O + NH_2NO$	300–3000	$1.0 \times 10^{-3} T^{3.3}$ exp($-14{,}800/T$)	119
$HNO_3 + HN_3 \rightarrow H_2O + NH_2NO_2$	300–3000	$4.3\ T^{3.5}$ exp($-22{,}140/T$)	a

[a] Original publications can be found in Ref. 112.

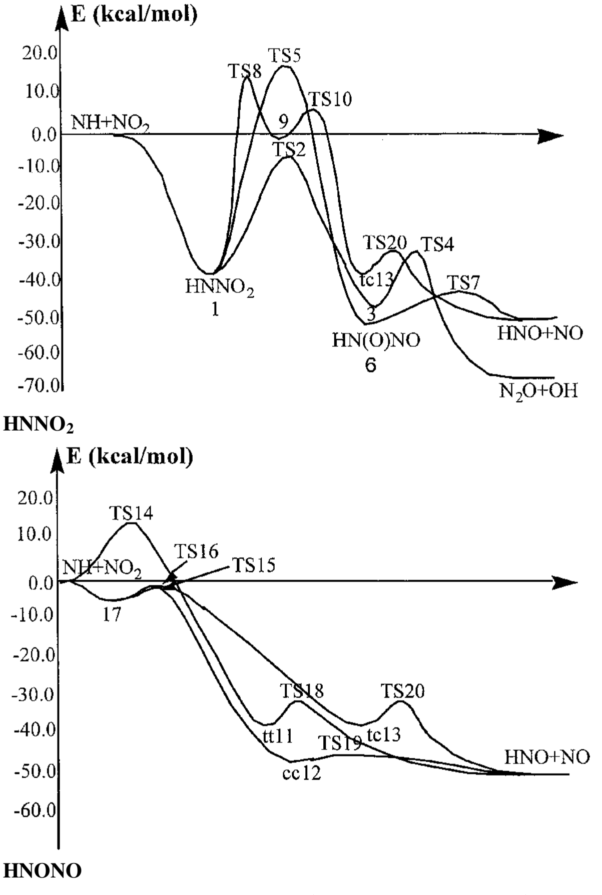


Fig. 2 Based on G2M calculation (see Ref. 119 for details) potential energy profiles for the reaction NH + NO_2 via.

can be incorporated into chemically based flame zone models of combustion.

V. Incorporating Kinetics and Mechanisms into Combustion Models

This section describes the approaches to explore, utilize, and model the different kinetic mechanisms that are used in modeling the combustion of a propellant ingredient. The combustion process of an energetic solid is a complex combination of reactions occurring within the burning surface (Sec. III) and the near-field gaseous phase (Sec. IV). General observations are that many propellant ingredients form a thin liquid layer on the surface during combustion. Condensed-phase reactions can occur in this liquid layer forming bubbles, in which gas reactions can also subsequently occur. Figure 3 is a schematic of the process showing the nonreacting solid on the left and progressing through the liquid layer and finally the gas. The process generates a very frothy mixture of liquid, bubbles, gas, and droplets, making the division between gas and condensed phases, that is, the burning "surface," difficult to define or measure. Also, the dimensions of the phases vary with pressure. For example, at 1 atm, the liquid layer is ~70 μm thick for HMX and ~130 μm for RDX, whereas the gas-phase reaches equilibrium within ~4 mm for HMX and ~1 mm for RDX (Refs. 121 and 122). At higher pressures (70–100 atm), the liquid layer is less than 20 μm thick, and the equilibrium temperature is reached within ~100–200 μm of the surface.

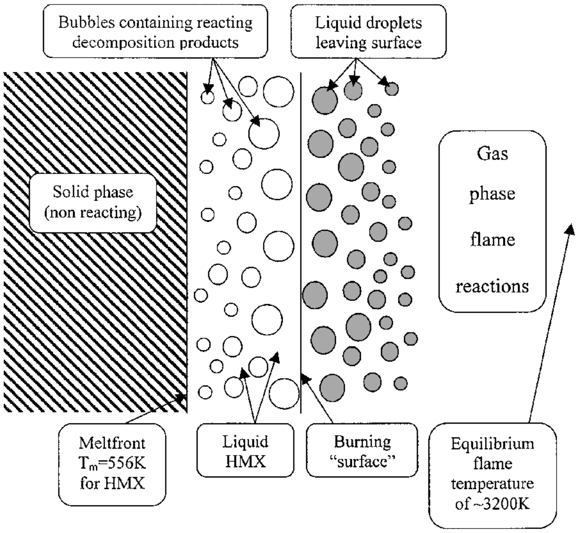


Fig. 3 Schematic of the physical processes occurring at the surface of a burning propellant ingredient.

Developing a mathematical model to describe the process in Fig. 3 is a great challenge. As discussed earlier, experimental data relating to the kinetics of the reactions occurring in the liquid layer along with the physical properties are very difficult to obtain due to the small size of the layer and the inherent transient nature of species. The reactions in the gas phase are more amenable to diagnosis because many of them can be measured independently or calculated by ab initio methods.

A. Utilization of Condensed-Phase Kinetics and Mechanisms

Both HMX and RDX have a relatively well-defined liquifaction temperatures (~280–283°C for HMX and ~205°C for RDX). Below the liquifaction point, it is usually assumed that solid-phase reactions can be neglected because the gas- and liquid-phase reactions are much faster than those in the solid phase. Above the liquifaction temperature, it is assumed that decomposition reactions begin and mark the start of the combustion process. Thus, in modeling the condensed-phase reactions, the process is normally initiated by an initial bond breaking reaction. This is generally the case, except for AP in which one modeling study concluded that solid-phase reactions had to be accounted for[123] to determine the observed combustion behavior. Also in the case of energetic polymers, such as GAP, the liquifaction point is not well defined. Thus, an arbitrary low temperature must be selected for modeling purposes to correspond to the onset of reactions.

The condensed phase processes discussed in Sec. III for HMX and RDX are described in more detail by Brill et al.[84] and involve primarily reactions (1–3). The final step added to the Brill et al. condensed-phase mechanism is the evaporation of the pure liquid propellant [reaction (13)]. This overall formalism has been used extensively in recent combustion models:

$$\mathrm{HMX(RDX)}_{(l)} \Rightarrow \mathrm{HMX(RDX)}_{(g)} \qquad (13)$$

Determining appropriate kinetic parameters for reaction steps is usually much more difficult than proposing reaction steps. To help define the kinetic parameters for reaction (2), Brill[84] proposed using kinetic data from a simple linear nitramine, dimethylnitramine (DMN), which decomposes to form NO_2 and HCN, similar to what is proposed for reaction (2). The rate parameters reported by Lloyd et al.[124] were reasoned to represent the best estimate of the N–NO_2 homolysis rate.

To evaluate the rate parameters for reaction (1), the T-jump/FTIR experiment was used to measure the species evolving from heated RDX and HMX samples.[69] This was necessary because there are no known simple nitramines that decompose only to N_2O and CH_2O. From these data, a N_2O/NO_2 ratio was determined for both RDX and HMX. To get the temperature dependence of reaction (1), Brill and Brush[69] proposed that the measured N_2O/NO_2 ratio should closely follow the ratio of the kinetic rate constant for reaction (1) to that of reaction (2). Therefore, the rate expression for reaction (2) and the measured N_2O/NO_2 ratio were used to determine the kinetic parameters for reaction (1).

Kinetic rate constants for reaction (3) (the heat-generating $CH_2O + NO_2$ reaction) have been determined by three different sources,[125–127] again with relatively large differences in the reported values. Brill[84] chose the kinetic rate parameters from Lin et al.[127] because their data covered the largest temperature interval. How to apply a gas-phase reaction within the condensed phase is a concern. If the decomposition products are treated as bubble-forming gases in the liquid phase, then the pressure inside the bubbles would be greater than the ambient pressure. It is not certain how great a pressure difference exists in these bubbles, and so the pressure is generally approximated as that of the ambient pressure.

The final step in the Brill mechanism[84] is the evaporation of the liquid RDX or HMX. Because both RDX and HMX react as they liquify, it is very difficult to get experimental vapor pressure data. However, solid–vapor equilibrium data, that is, sublimation data, are reported for RDX (Refs. 128–130) and HMX (Refs. 128, 129, and 131). When the heat of sublimation and the Van't Hoff equation are used, the vapor pressure of HMX and RDX can be approximated for conditions above the liquifaction temperature (see Ref. 132). The vapor pressure of RDX is observed to be several orders of magnitude higher than that of HMX, and, thus, it can be expected to vaporize much more readily than HMX. Within the calculations using the condensed-phase mechanism, the evaporation step is much more predominant in RDX than in HMX.

Analogous condensed-phase mechanisms have been developed in conjunction with models for AP, GAP, ADN, and various combinations of ingredients as described in Sec. III.

B. Utilization of Gas-Phase Mechanisms

During the past two decades extensive progress has been made in the development of detailed gas-phase mechanisms for combustion processes,[133] so much so that a standard mechanism for hydrocarbon (methane or natural gas) combustion with 325 steps and 53 species can be downloaded from the web. This is the Gas Research Institute (GRI) mechanism.[134] Parallel to the development of the hydrocarbon mechanism, work has proceeded to develop analogous mechanisms for propellant ingredients. The most extensive is work that was initiated by Melius and Brinkley[135] and Melius[136,137] during 1986–1990 for RDX. This work was expanded by Yetter et al.[138] culminating in a standard mechanism for RDX published in 1995 and consisting of 232 reaction steps and 45 species.[139] The Yetter et al.[138] mechanism has provided the basis for most of the recent advancements on modeling of burning RDX. Both the hydrocarbon and the propellant work utilize the CHEMKIN format and libraries,[140–142] which have become standards for analyzing multistep gas-phase chemical reactions. Mechanisms have been developed for HMX, AP, GAP, ADN, and some combinations of ingredients.

The reaction species leaving the burning surface are usually relatively complex, that is, three or more atoms. Further from the surface, as the reactions approach equilibrium, the reactants and reactions become typical of combustion in general, that is, species such as NO, OH, N_2O, CO, etc. Reactions involving many of these species are also involved in hydrocarbon combustion and many can be found in the GRI mechanism. The difficult work that remains is in characterizing the condensed-phase and the near-surface reactions as discussed.

VI. Conclusion

The purpose of this paper is to bring the community of chemists and engineers studying solid propellants abreast with fundamental chemical research conducted recently on the surface reaction zone and aimed at full-scale combustion modeling. Clearly, we are not at the prediction stage where we can do without experimental measurements. Nevertheless, through a team effort in the past six years considerable progress has been made on the very difficult problem of defining and incorporating chemical mechanisms of the heterogeneous surface region into the propellant combustion modeling.

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