PHRENOLOGICAL AND MECHANICAL STUDY OF SOLID PROPELLANT
DARK ZONE EXPERIMENTS

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ABSTRACT

The dark zone (DZ) region is a curious phenomenon in low pressure (~5 – 100 atm) flames of combusting solid propellants. The chemistry controlling low pressure DZ structure has recently been shown to be crucial to combustion properties of these propellants at higher pressures, as in guns. The present work focuses on quantitative testing of a model of DZ structure based on a detailed chemical mechanism. A critical survey of the literature was performed to find sufficiently complete experimental datasets. Modeling then was performed, comparing predicted DZ ignition delay times, $\tau_{DZ}$, from the model with experimental results obtained by converting the DZ lengths to corresponding times for convective flow. Predictions were mostly within a factor of two of experiment. Most can be made to agree by changes of initial DZ temperature input to the model within the error limits of measured temperature values. The model captures the proper trends with pressure and DZ mixture ratio. However, many of the predicted $\tau_{DZ}$ results were too long, and few too short, a concern that is discussed. Work which could elucidate whether there might be an important mechanism error and key reactions within the DZ are briefly discussed.

1. INTRODUCTION

One of the most curious facets of solid propellant combustion is that at low pressures (~5 – 100 atm) many nitrate ester and nitramine propellants produce a so-called ‘dark zone’ (DZ). This is a gas phase region between the solid propellant surface and high temperature luminous flame that emits little visible radiation. A schematic diagram in Fig. 1 illustrates the phenomenon. A solid, cylindrical propellant strand is made to combust at one end. A DZ can occur as a non-luminous region just above the surface. For nitrate esters the DZ consists primarily of $H_2$, $H_2O$, $N_2$, NO, CO, and CO$_2$; for nitramines, in addition to these species, HCN and, often, important traces of N$_2$O and NH$_3$ are also present. Typically a luminous flame appears above the DZ. The DZ is believed to form due to conversion of initially formed gas phase components in the first stage flame to a mixture containing NO and HCN intermediates. These intermediates react very slowly with the other mixture components, retarding the energy release. The final temperature is not reached until these intermediates are converted to final products, e.g. N$_2$, H$_2$O, CO, and CO$_2$. Thus an intermediate DZ temperature typically in the 1200 – 1600 K range is reached. At some time after its initial formation, the DZ mixture rapidly reacts forming a second stage flame. This flame converts the mixture to near-equilibrium products and raises the temperature close to the adiabatic limit, typically in the 2200 – 3200 K range. The delay time between the initial DZ mixture formation and the second stage reaction is termed ‘DZ ignition delay’, $\tau_{DZ}$, a property of the DZ chemical mixture at the relevant conditions. The effect of this delay, coupled with convective motion of the DZ gaseous mixture, causes formation of the nonluminous DZ region between the propellant and luminous flame.

Over the past ~20 years we have at various times studied the DZ phenomenon, but due to becoming involved in endeavors perceived to be more important, never finished our efforts on this issue. The chemistry taking place in the DZ was not perceived to be important to the overall combustion process because the second stage flame occurs far from the surface, so that its heat release would not influence the condensed phase gasification rate; this appears to be true for low pressure conditions where the DZ is long. However, recent solid propellant combustion modeling has made it clear that the chemistry that controls the length of the DZ at low pressure is much more important to high pressure combustion, especially the burning rates, than anyone has previously appreciated for both nitrate ester and nitramine propellants. It has thus become clear that models used for formulation guidance and interior ballistics codes require testing of DZ chemistry. Newly motivated, we reinstituted study of the DZ phenomenon with emphasis on quantitative results. We present a brief synopsis; more details will appear elsewhere.

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* The exact equilibrium conditions only occur downstream in the burnt gas (luminous flame) region after radical concentrations have time to adjust to their equilibrium values.
Critical Evaluation And Modeling Of Solid Propellant Dark Zone Experiments

2. MODELING APPROACH

2.1 Analysis of Experiments; Modeling Physics and Codes

The most important features of a DZ are its length and the closely related $\tau_{DZ}$. One could predict the entire propellant flame structure, including the first stage flame, using steady-state flame models, e.g. Refs. 6,7. However, there is a great deal of uncertainty regarding the near-surface and first stage flame regions in all results. In particular, the uncertainty originates from lack of reliable means to determine condensed phase reactions and/or nascent gas phase species produced, and, thus, into what initial DZ mixture they might evolve. Modeling of the entire burning structure is therefore not a good approach to test the DZ portion of the combustion and chemical mechanism. A simplified approach\(^8\) allows us to instead use information about initial DZ mixture conditions obtained from experiments to test the DZ mechanism independently from events in the surface and near surface regions. Key assumptions are that diffusion and thermal conduction are negligible. These assumptions yield a so-called 'plug-flow' model. Assuming temperature and mixture ratio are constant in the DZ, $\tau_{DZ}$ is recognized as the time for gas convection through the DZ region of length $L_{DZ}$:

$$\tau_{DZ} = L_{DZ}/v$$  \hspace{1cm} (1)

where $v$ is the convective flow velocity. The flow velocity may be obtained from the continuity equation across the condensed phase - gaseous boundary:

$$v = r_b \rho_s/\rho_g,$$  \hspace{1cm} (2)

where $r_b$ is the solid propellant burning rate, and $\rho_s$ and $\rho_g$ are the solid and gas phase mixture densities, respectively. Combining these with the ideal gas law, one obtains:

$$\tau_{DZ} = L_{DZ} MP/RT_{DZ} r_b \rho_s$$  \hspace{1cm} (3)

where $R$ is the ideal gas constant, $M$ is the average molecular weight of the DZ gas mixture, and $T_{DZ}$ is the measured DZ temperature. Eq. 3 is used to analyze experimental data to obtain measured $\tau_{DZ}$ values.

To model the DZ structure using this approach, one first needs an appropriate mechanism. In addition, the following data are needed from experiment: initial DZ temperature and mixture ratio, DZ length, and propellant density and burning rate at pressure of interest. A time-dependent reactor code can then be used; we choose SENKIN.\(^{10}\) We start with the initial conditions of temperature and mixture ratio of the DZ from the experiments and calculate the evolution of the mixture.

Constant pressure, adiabatic conditions are assumed. The model predicts majority species and temperature remain approximately constant at plateau values, while important trace radical species increase dramatically, until a chemical runaway is reached. The mixture then rapidly converts to nearly equilibrium products and the temperature is nearly adiabatic - slight variance from equilibrium is, of course, observed due to the radical pool concentration having to adjust slightly in the burnt gas (luminous flame) region. We define the runaway point as the time when the chemical heat release rate reaches its maximum value. This computed time can then be compared to measured $\tau_{DZ}$ values.

2.2 Chemical Mechanism

The mechanism developed in the present work was obtained by starting with the mechanism of 59 species, 365 chemical reactions used by Miller and Anderson\(^6\) to model nitrate ester solid propellant combustion; reactions pertinent to HCN combustion were included, so that the mechanism is also appropriate for nitramine DZs (tracing back over many revisions/versions, the initial basis of the Ref. 6 mechanism was, in fact, our original DZ mechanism, used in Ref. 1 for both propellant types). We have recently updated this mechanism by incorporating revisions from literature survey to 5 species heats of formation and to 34 reactions. The most recent mechanism, including species thermodynamics, will be presented in the detailed report in preparation.\(^8\)

3. CRITICAL SELECTION OF EXPERIMENTAL DATASETS

One of the most important aspects of the present work has been a critical assessment of studies from the literature to select appropriate test datasets. As mentioned in section 2.1, one needs the following data from experiment: initial DZ temperature and mixture ratio, DZ length, and the solid propellant's density and burning rate at the pressure of interest. All the relevant experiments involved single propellant strands burning at constant pressure at one end, i.e. in cigarette fashion. A variety of diagnostics were used in these experiments. The accepted datasets are restricted by several criteria and consistency tests judged to be very important: (1) species and temperature profile data obtained from well-established measurement techniques and having good S/N characteristics, e.g. profiles must be reasonably smooth, indicative of reasonably low-flicker, steady flame character; (2) if available, check photographs that the flame appears one-dimensional, laminar, and its area is reasonably constant in the vertical direction; (3) atomic mass balance within the DZ reflects that of the propellant; (4) the dataset survives energy closure testing. Energy closure testing means the enthalpy of the DZ mixture
matches that of the initial propellant, as tested by predicting adiabatic flame temperatures of both the propellant and the measured DZ mixture to see if these match. All of these various tests could not be examined for all the datasets for a variety of reasons. The various tests were required to be met insofar as it was possible to perform them, and a few promising cases had to be discarded for the present, quantitative testing purposes (see Ref. 8).

With these considerations, we found four studies on nitrate ester propellants\textsuperscript{11-14} and two on nitramine propellants\textsuperscript{15,16} which provide the necessary data and meet the above tests. Details on all those retained, any estimates made for missing data, and some candidates which were discarded, are not discussed further here, but will be in the report in preparation.\textsuperscript{8} Three of the nitrate ester studies were performed for a variety of pressures. Comparisons of the $\tau_{DZ}$ values inferred from the experiments to our predictions and discussion of the chemical features is given in the next section. The present version is very condensed due to the length limit.

4. RESULTS AND DISCUSSION

An example of predicted DZ structure as function of time is shown in Fig. 2; the time correlates, approximately proportionally, to distance along the flow in the DZ of the corresponding propellant flame. Conditions correspond to JA2 propellant, as studied in the DZ of the corresponding propellant flame. However, their propellant ‘EC-1’ contains only small amounts of the additives and has NC/NG ratios similar to HG55’s mixture referred to as ‘PL673’. A number of nitrate ester DZ studies, e.g. HG55 and Vanderhoff and coworkers,\textsuperscript{13} have shown that DZ mixture compositions do not vary strongly between similar nitrate ester propellants, nor vs. pressure. Therefore, to model this data, we assumed the DZ mixture composition of HG55’s EC-1 is the same as that for PL673. Experimental $\tau_{DZ}$ values are all large compared to experimental results.

Aoki and Kubota\textsuperscript{12} (AK82) studied 12 double base propellants composed primarily of NC and NG and small amounts of two additives, diethylphthalate (DEP) and 2-nitrodiphenylamine (2-NDPA). Photography and thermocouple techniques were used to measure $r_b$, $T_{DZ}$, and $L_{DZ}$. No species measurements were made. However, their propellant ‘EC-1’ contains only small amounts of the additives and has NC/NG ratios similar to HG55’s mixture referred to as ‘PL673’. A number of nitrate ester DZ studies, e.g. HG55 and Vanderhoff and coworkers, have shown that DZ mixture compositions do not vary strongly between similar nitrate ester propellants, nor vs. pressure. Therefore, to model this data, we assumed the DZ mixture composition of HG55’s EC-1 is the same as that for PL673. Experimental $\tau_{DZ}$ values are all large compared to experimental results.

Vanderhoff and coworkers\textsuperscript{13} (VKMT92+97) performed studies on JA2, a fielded military propellant consisting primarily of the three nitrate esters NC, NG, and DEGDN (diethylene glycol dinitrate) with some trace additives. Measurements from the studies were combined to obtain a test case at 16 atm. Ultraviolet absorption spectroscopy was used to measure NO and some radical concentrations and temperature, while infrared absorption spectroscopy was used for NO, CO, CO$_2$ and H$_2$O, all at

\begin{itemize}
  \item Overlooked physical effects could alternatively be responsible.
\end{itemize}
10 atm. $L_{\text{DZ}}$ was obtained from figures in the study at 16 atm, and it was assumed the DZ mixture ratio does not vary vs. pressure to obtain a 16 atm test case. Measurements performed on a few DZ species concentrations vs. pressure support this assumption. The experimental data yield a measured $\tau_{\text{DZ}}$ of $6.5 \pm 0.8$ msec.

With the nominal measured inputs, the predicted value is 9.3 msec, or about a factor of 1.4 too long. Note the predicted species and temperature profiles for this case were used in Fig. 2 as an example of typical model results. Increasing the input $T_{\text{DZ}}$, nominally 1500K, by the approximate error limits to 1550K, yields a predicted value of 7.0 msec, in excellent agreement with the measured value. The profile plots remain qualitatively similar to Fig. 2 (not shown).

Parr and Hanson-Parr$^{14}$ (P+HP02-BTTN) studied combustion of 1,2,4 butanetriol trinitrate (BTTN), a liquid nitrate ester compound similar in structure to nitroglycerine, in the range 0.92 – 51.0 atm. $L_{\text{DZ}}$ could be determined in the more limited range 10.0 – 20.4 atm. A tube-type burner system with constantly fed BTTN was used. Temperatures and species concentration profiles were measured via a combination of thermocouple and Raman spectroscopy techniques. Measured and predicted $\tau_{\text{DZ}}$ values are compared in Fig. 5. As can be seen, the agreement is excellent for most pressures. However, for reasons which will be discussed in more detail later, the error limits of input temperatures are larger than in the other test cases, likely about 100K, so the predictions have even larger uncertainty than the ‘+50K’ results of Fig. 5 indicate.

Litzinger et al$^{15}$ (LLT00) provided the first of the two nitramine cases. They studied several nitramine/energetic binder propellants at 1 atm using molecular beam – mass spectrometric (MBMS) sampling and thermocouple techniques. The case retained was for a RDX/BAMO propellant. The $\tau_{\text{DZ}}$ value inferred from the measurements is $0.24 \pm 0.7$ msec. With the nominal best measured values used as model inputs, including $T_{\text{DZ}} = 1500 \pm 150$K, we obtain 0.56 msec, which is a little over a factor of 2 longer. However, using $T_{\text{DZ}} = 1600$K, we obtain 0.23 msec, in good agreement with the measured value. The nitramine DZ results, like the nitrate esters, have a very high sensitivity to the assumed initial temperature. Unlike the other nitramine case (next paragraph), in this case a trace of NH$_3$, ~ 0.01 mole fraction, was observed in the DZ. Sensitivity analysis, discussed briefly below, indicates reactions of N$_2$O and of NH$_3$ species derived from the NH$_3$ are very sensitive during the DZ ignition delay. Therefore to examine the sensitivity to initial N$_2$O, we increased it from 0.04 to 0.06 mole fraction, other inputs remaining at their nominal values. The result was 0.33 msec, which is nearly within error limits of the measured value. To examine the sensitivity to initial NH$_3$ mole fraction, we removed it, resulting in 0.83 msec, and alternatively increased it to 0.015, resulting in 0.48 msec. These results confirm high, positive sensitivities of the overall chemical rates to either initial N$_2$O or NH$_3$. Similar tests on H$_2$, which is also present as a trace component, with very wide relative error limits due to a noisy profile, indicate initial H$_2$ sensitivity is negative, but very small; it apparently contributes little to radical pool formation, whereas the effect of N$_2$O or NH$_3$ as precursors to radicals is strong (vide infra). However, although the amount of NH$_3$ is small, its experimental profile is relatively noise-free, so increasing the value this much may not be justified. Thus, error limits in the measured temperature or N$_2$O concentration might account for the difference in observed and computed $\tau_{\text{DZ}}$ results, but the random error in the NH$_3$ concentration in and of itself perhaps cannot.

The second nitramine test case was obtained from Parr and Hanson-Parr$^{16}$ (PHP02/04-HMX) based on an HMX/GAP/BTTN propellant combusting at 0.92 atm. The measured species include traces of CH$_2$O and C$_2$H$_4$ whose error limits are large. We inferred $\tau_{\text{DZ}}$ from the measurements as 0.88±0.27 msec. With the nominal measured input parameters, including $T_{\text{DZ}} = 1450$K, our predicted $\tau_{\text{DZ}}$ is 3.54 msec. If the above two trace species are removed (conceivably correct considering the error limits and difficulty deciding where the first stage flame ends and DZ begins), the result is 1.74 msec. Including those trace species, but increasing $T_{\text{DZ}}$ to its upper error limit of 1550K, the result is 1.23 msec, almost within error limits of the measured result. Removing the trace species and using 1550K, the result is 0.64 msec. These authors did not observe any NH$_3$, as in the preceding nitramine case; one would expect their techniques to be sensitive to NH$_3$, strongly suggesting this is a credible key difference between DZs of these propellants. However, PHP02/04-HMX did also observe traces of N$_2$O. The nominal value in the DZ appears to be about 0.04 mole fraction. However, their N$_2$O profile varies considerably throughout the flame (see Fig. 12, Ref. 16) and there is considerable scatter about the trend. Use of 0.06 mole fraction for N$_2$O, with otherwise nominal measured input parameters, leads to $\tau_{\text{DZ}}$ of 1.90 msec. This change apparently is not, by itself, sufficient to explain the difference vs. experiment, but like the RDX case above, demonstrates a high sensitivity to this parameter.

In general, the model seems to be a fairly good representation of the major qualitative features of experimental DZ structure for both nitrate ester and nitramine propellants. The quantitative comparisons show the predictions are all within a minor change of input parameters, especially DZ temperature, of reproducing experimental results within their error limits. It is especially important to note the predicted $\tau_{\text{DZ}}$ results...
follow experimental trends vs. changes in formulation, which causes some minor variation in $\tau_{DZ}$ results; and vs. pressure for nitrate esters where data were available, for which the changes are much larger. It is rather discomforting, however, that in many cases the predicted $\tau_{DZ}$ results, although within error limits of a key input parameter, are too large vs. experiment. Therefore, one must consider the possibility that some important factor is missing in the model. There are a number of physical effects that could account for the differences, discussed in detail elsewhere. However, it must be admitted that there remains a very real possibility that there is some important point being missed in the detailed chemical mechanism; the derivation and testing of this mechanism has been the major focus of the present - and continuous over nearly 20 years - effort. Since magnitudes of the differences are similar in the cases in question, one might speculate that the hypothetical error affects both nitrate ester and nitramine propellant DZ models equally; if so, if found and corrected, it would improve predictions for both. An obvious possibility is that some radical chain initiation or branching reaction is missing. Key thermodynamics parameters can also have significant effects, so need examination, too. There is an extremely large number of possible reactions and thermodynamics parameters to investigate; the mechanism may be the wrong avenue to pursue anyway because, as discussed above, the problem may be an overlooked physical effect. Or, it may be that there is no problem at all, and the one-directional disagreements are simply the result of serendipity coupled with a statistically small number of cases.

The observations of the last paragraph lead naturally to a discussion of what future efforts might best contribute to improvement of the model. Clearly it would help to have more DZ measurements. There are several cases available for nitrate ester propellants over fairly wide pressure ranges so, unless the precision of measurements can be improved considerably or DZ mixture ratios greatly changed, more than one or two further efforts are probably not justified if simply for the goal of studying the DZ structure. For nitramine propellants, there is a dearth of data. It would be especially helpful to have studies over wide pressure ranges; furthermore it is important to establish whether the DZ mixture ratio is constant vs. pressure for nitramine propellants. Although several of the nitrate ester studies establish this is true for that propellant type, it might well not be so for nitramines, especially since pyrolysis studies on the nitramines RDX and HMX establish a condensed phase temperature dependence for the nascent gas phase HCN/CH$_3$O ratio produced.\textsuperscript{11}

It is important to note that our impression, having completed this study, is that one can only expect to obtain a semi-quantitative chemical mechanism test from these types of experiments. The experiments provide valuable information about what species are present in the DZs, and approximate results for their concentrations and the temperature. Modeling with a detailed mechanism can reveal key reactions and species controlling the structure, at least insofar as best mechanisms predict. However, these experiments cannot be regarded as very stringent quantitative tests of, or perhaps even very good methods for elucidation of, a chemical mechanism. The measured concentrations and temperatures needed for model input parameters are simply not precise enough, and probably cannot be made precise enough. What is needed are more controlled kinetics experiments starting with gaseous mixtures similar to those observed in the propellant studies. The most obvious technique to try is shock tube experiments, although some of the $\tau_{DZ}$ values observed for DZ mixtures might be slightly larger than can typically be used in such work. Mixture ratios can be very precisely known and readily controlled in shock tube experiments, much better than in propellant combustion, because of well-established preparation techniques - recognizing that quantitative introduction of H$_2$O vapor would likely require more elaborate techniques than usual. Temperatures after passage of a shock are also more precisely known; although there might be some problems for this application due to similar rates of vibrational energy equilibration and reaction times since DZ mixtures are composed entirely of multiple-atomic species rather than the monatomic inert gas bath used in more typical shock experiments. If these problems could be overcome, such studies could yield very stringent tests of the mechanism. A particularly intriguing aspect is that the DZ mixture ratio could readily be varied, something which might only be crudely done via formulation changes, if at all, in propellant experiments. Variation of mixture ratio would allow determination of species reaction orders for the ignition delay time and/or global reaction rate. Such data typically yield the most delicate, stringent mechanism tests known. A serious mechanism error probably could not escape notice if measured reaction orders for the various species were established.

To close out this section, we briefly discuss some of the key reactions – and species – our detailed analysis of the chemical rates/pathways and sensitivities has revealed for our current best results. This may help guide future efforts at mechanism refinements, and in any case is certainly of scientific interest. More details will be presented in Ref. 8.

For nitrate esters, the JA2 case of VKMT92+97 is well-representative. Analysis of reaction rate coefficient temperature sensitivities indicates that during the ignition delay, the most sensitive reaction by far is:

$$\text{HNO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{OH} \quad (R1)$$
The following are also sensitive, but less so by about a factor of five:

\[
\begin{align*}
N_2O (+M) & \rightarrow N_2 + O (+M) \quad (R2) \\
H + HNO & \rightarrow H_2 + NO \quad (R3)
\end{align*}
\]

All these reactions are apparently sensitive because they affect the radical pool. The first two have positive temperature sensitivities and create radicals, while the last one has a negative sensitivity because it destroys a radical. R1 is the main radical source reaction. Tests show that changing the R1 rate coefficient’s A-factor has a very strong, inversely proportional, effect on computed \( \tau_{DZ} \), and thus \( L_{DZ} \), results for nitrate esters.\(^8\)

For nitramines, R1 plays a role, but is much less sensitive. The most sensitive reactions controlling the predicted \( \tau_{DZ} \) are instead:

\[
\begin{align*}
N_2O (+M) & \rightarrow N_2 + O (+M) \quad (R2) \\
N_2 + H & \rightarrow N_2 + OH \quad (R4) \\
H + HNO & \rightarrow H_2 + NO \quad (R3) \\
NH_2 + NO & \rightarrow NNH + OH \quad (R5) \\
NH_2 + NO & \rightarrow N_2 + H_2O \quad (R6)
\end{align*}
\]

where R2, R4, and R5 have positive, and R3 and R6 negative, temperature sensitivities. Most of these reactions affect the radical growth, the positive ones creating, the negative ones destroying, a radical. The one exception is R4. However, this reaction is highly exothermic, contributing strongly to the temperature increase and probably explaining its high sensitivity. The NH\(_2\) reactions tend to be relatively more sensitive for the LLT00 case than PHP02/04-HMX, apparently because of the presence of NH\(_3\) in the DZ initial mixture for the former and not the latter. NH\(_3\) is a precursor for NH\(_2\) via H abstraction by H and OH. The positive sensitivity of R5 outweighs the negative sensitivity of R6, accounting for the large increase in global reaction rate upon increase of NH\(_3\) fraction in the LLT00 case (and vice versa). In later stages of the nitramine DZ ignition delay period, reactions connected with HCN consumption also become important, including two on a major pathway:

\[
\begin{align*}
HNC + OH & \rightarrow HNCO + H \quad (R7) \\
HNCO + H & \rightarrow NH_2 + CO. \quad (R8)
\end{align*}
\]

R7 and R8 have positive temperature sensitivities; the HNC comes from unimolecular rearrangement of HCN. Note that NH\(_2\) thus can arise from the decomposition of HCN as well as NH\(_3\).

5. CONCLUSIONS

Because recent work has shown low pressure (~5 – 100atm) propellant DZ chemistry is much more important for high pressure (gun relevant) burning rates than has been previously realized, our interest in the DZ submodel we use in propellant combustion modeling has recently been rekindled. We have completed a thorough critical review of the literature and found six experimental studies yield data suitable for testing our DZ model. Comparisons of measured and experimental DZ ignition delay times, \( \tau_{DZ} \), were presented for these cases. For many cases, the predicted \( \tau_{DZ} \) results are slightly long vs. experiment (global reaction rate thus too slow). For all cases, the predicted \( \tau_{DZ} \) is subject to considerable error due to high sensitivity of results within precision limits of the input parameters. It is possible to make nearly all predictions agree with experiment by upwards adjustment, within error limits, of assumed initial DZ temperature. The trends vs. pressure, DZ mixture ratio, and, to the extent of study, propellant formulation, are well-reproduced. The level of agreement obtained is therefore fairly good. However, it must be admitted there is some concern that there may be an important physical or chemical effect not taken into account in the model. Possible types of future studies which might contribute further to our understanding and perhaps elucidate whether there is indeed something being missed in the chemistry part of the present model were discussed.

REFERENCES


Fig. 1. Idealized schematic of a burning solid propellant strand with a dark zone. In typical experiments, the strand is oriented vertically, but it is shown rotated 90° clockwise here to make the correlation to the temperature profile clear.

![Diagram of burning solid propellant strand with dark zone and temperature profile](attachment://diagram.png)
Fig. 2. Predicted temperature and major species profiles for the dark zone region of JA2 propellant at 16 atm. Conditions correspond to Vanderhoff and coworkers’ experiment\textsuperscript{13} (see text). For initial conditions, the calculation uses measured values from the experiment just above the point where the first stage combustion, which is near the propellant surface, is complete; this explains why the first stage flame is not shown.

Fig. 3. Comparison of experimental and predicted DZ ignition delay times for Heller and Gordon NG/NC nitrate ester propellant (Experiment, HG55, Ref. 11; Calculated, this work).

Fig. 4. Comparison of experimental and predicted DZ ignition delay times for Aoki and Kubota double base propellant (Experiment, AK82, Ref. 12; Calculated, this work).

Fig. 5. Comparison of experimental and predicted DZ ignition delay times for Parr and Hanson-Parr BTTN nitrate ester propellant (Experiment, P+HP02-BTTN, Ref. 14; Calculated, this work).