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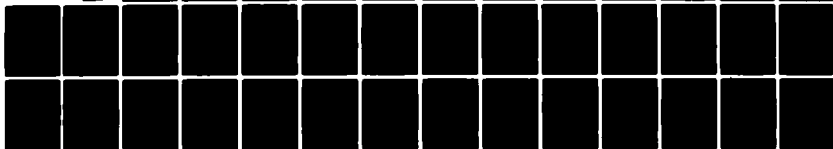
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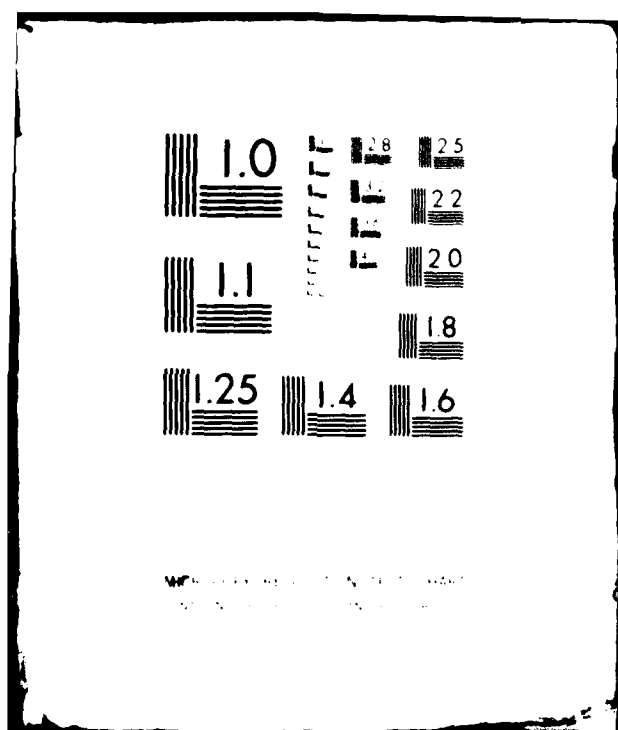
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MEMORANDUM REPORT ARBRL-MR-03005

THE ARO WORKING GROUP MEETING
ON IGNITION PROCESSES, JUNE 1978

David R. Crosley
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March 1980

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (clt) A working group meeting was held at the Ballistic Research Laboratory on 15, 16 June 1978, under sponsorship of the Army Research Office, Durham. The general topic of discussion was ignition and combustion of propellants with a view toward development of an understanding from a microscopic basis, with particular emphasis on the influence of chemistry. The format of the workshop was unusual in that it was, by design, predominantly free discussion with little formal presentation scheduled, and closed attendance. Scientists from diverse areas (Cont'd)		

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10. Abstract (Cont'd)

related to propellant studies were invited; these specialities were thermal decomposition of propellants, gas phase chemical kinetics, investigations of solid propellant combustion diagnostics, and modeling. This report is a lightly-edited transcript of the proceedings. It also presents some views on the success of the workshop format.

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I. THE STRUCTURE OF THE WORKSHOP

A. Workshop Purpose

The overall mechanism by which solid propellants ignite and burn, forming the hot product gases needed for propulsive thrust, involves a wide variety of physical and chemical processes. In addition, the actual burning of propellants can be carried out only under relatively harsh conditions not conducive to carefully controlled and reproducible experiments able to isolate some aspect of the mechanism for detailed study. Consequently, much of the picture of such combustion is comprised of a (usually) reasonable but untested linking of results from studies of subprocesses. These separate studies are conducted under more tractable experimental conditions so that the results per se are valid; however the necessity of such an approach forms a barrier to a clean assessment of relative contributions under real-propellant conditions. It also leads to the conduction of research on pieces of the puzzle by scientists with diverse enough backgrounds that little meaningful interaction may result.

A Working Group Meeting on Ignition Processes sponsored by the Army Research Office through Dr. David R. Squire of the Chemical and Biological Sciences Division, was held at the Ballistic Research Laboratory on 15 and 16 June 1978. A limited number of productive and imaginative scientists in several disciplines related to propellant combustion were brought together for a meeting with predominantly open-discussion format and closed attendance. Specializations represented were: ignition processes, thermal decomposition, chemical kinetics, and modeling. Some participants had little or no experience with propellants per se. The workshop attendees are listed in Table I.

The stated purpose of the meeting was to address the issue of how studies of propellant thermal decomposition, and knowledge of gas phase chemistry, are related to propellant combustion. Key sub-questions included: What constraints on a melding of the subprocesses are imposed by data and observation on actual propellants burning under "real" conditions? What experiments have been performed, or could be carried out, to settle some of the many ambiguities in interpreting relative importance and contributions? The complexity of the overall problem dictates linking of the various aspects by simulation models; how can these be used effectively and be based on sound fundamental mechanisms?

B. Workshop Format

The workshop was unusual in that a limited number of participants were invited, and only those invited were admitted. The intent was a loosely structured conversation among peers, with us observers to serve as our audience for "presentations" nor to inhibit honest discussions about problems which might go unmentioned at a conventional meeting. Only a few talks were planned; two-thirds of the meeting time was free

TABLE I. WORKSHOP PARTICIPANTS

<u>Participant</u>	<u>Affiliation</u>	<u>Address</u>
(Invited Participants)		
Arthur Axeworthy	Rocketdyne	Canoga Park, CA
Sidney Benson	Univ. of So. CA	Los Angeles, CA
Leonard Caveny	Princeton Univ.	Princeton, NJ
Michael Cowperthwaite	SRI International	Menlo Park, CA
William Gardiner	Univ. of Texas	Austin, TX
Irving Glassman	Princeton Univ.	Princeton, NJ
David Golden	SRI International	Menlo Park, CA
John Hastie	NBS	Gaithersburg, MD
Bruce Isom	Hercules Inc.	Magna, UT
Takashi Kashiwagi	NBS	Gaithersburg, MD
Douglas Kooker	ARRADCOM, BRL	APG, MD
Howard Palmer	PA State Univ.	University Park, PA
Kevin White	ARRADCOM, BRL	APG, MD
Forman Williams	Univ. of CA at San Diego	La Jolla, CA
(Army Organizers and Attendees)		
David Crosley	ARRADCOM, BRL	APG, MD
David Downs	ARRADCOM, LCWSL	Dover, NJ
Robert Fifer	ARRADCOM, BRL	APG, MD
George Keller	ARRADCOM, BRL	APG, MD
Fred Schmiedeshoff	Army Research Office	Durham, NC
David Squire	Army Research Office	Durham, NC

for discussion. The choice of participants was highly subjective, and it should be noted that those responsible for the final selection (Crosley and Fifer) are aware that there are many more workers who have participated and made valuable contributions.

C. Report Format

The attendees were assured that, except for the "talks", all recording of discussions would omit names. Thus this report is a loosely-edited transcript of the proceedings of the workshop. The authors have attempted to transmit the ideas discussed as faithfully as is possible without endangering understandability. Thus the material is presented chronologically, and there is no summary by the authors.

II. THURSDAY MORNING

The workshop began with some brief opening remarks by Crosley, Fifer and Squire repeating comments made earlier to each participant by phone and in a letter (see Appendix A) concerning the general spirit of the meeting. The comments were essentially as follows: Given the background of those participating, it is obvious that what is desired in this meeting is emphasis on the microscopic mechanisms responsible for propellant ignition and combustion. Several areas represented by different participants all contribute to an understanding of the overall mechanism: thermal decomposition studies (presumably) yield information on the starting gas-phase reactants; data exist concerning the "real" behavior. For the most part, chemistry in any detailed way is left out of present propellant and ignition descriptions. Since ignition criteria depend on pressure, one knows that gas-phase chemistry is indeed of some importance. Here we have assembled some experts in the kind of chemistry which should be pertinent to propellant combustion. How can this field contribute to an understanding of, and perhaps an unraveling of, the relative importance of different mechanisms present in propellant combustion? What kinds of experiments exist which can shed some light on how these several aspects should be put together? What experiments are prime candidates for trial so as to answer some of the important questions? What are some of the final actual observations on propellant combustion that form necessary constraints on any picture developed from a combination of subprocesses and mechanisms? Given that the problem is of such complexity that modeling is required to tie together the various pieces, how can this be most fruitfully accomplished? Finally, how can the models be made to yield the most insight into the microscopic processes responsible, yet still computationally tractable and realistic in their description of the overall process?

White then presented a talk describing some Army problems with propellant ignition and combustion for which a better fundamental understanding of the processes involved is needed. This talk elicited considerably more comment, interruptions, and questions than anticipated

by the organizers. We feel this was demonstrative of some real natural curiosity and inquisitiveness on the part of the participants when confronted with an interesting and challenging problem regardless of its degree of applied vs. fundamental aspects.

White pointed out that one problem of concern is the sensitivity of ignition (in the sense of field requirements) to the ambient temperature. This was used by him as a vehicle to describe the actual operation of a gun and to furnish a feel for the time and distance scales involved, information which was useful to a number of participants. The actual granular solid propellant in a charge burns in several milliseconds, which includes the time for flame spread through the granular solid bed. If the ignition of the propellant along the chamber axis is not really isochronic, longitudinal pressure waves may be created whose amplitude may grow beyond the gun's design criteria, leading to a catastrophic failure.

In many gun systems ignition is carried out these days using black powder, which remains an extremely useful igniter even though we now have large numbers of synthetic compounds. One of the reasons that no superior substitute for black powder has been found is that the actual mechanisms by which it works are not well known, so that it is difficult to design a substitute which one can expect to have its desirable qualities but lack the undesirable ones. One of the main reasons black powder is so useful is that it spreads the flame very quickly and with little pressure dependence, so that the propellant is ignited evenly and smoothly (the black powder is a core coaxial to the cylindrical granular propellant bed; one wishes to have the propellant ignite radially with no longitudinal gradients along the core, and this is why speed in the igniter itself is of importance).

One of the problems with black powder is its variability. The speed with which it fully ignites (about 70 msec is the average time for a large caliber gun) may differ by factors of 3-4. It is an open question why this variability exists. Black powder is hardly a simple chemical compound but a complex mixture which can vary greatly from manufacturer to manufacturer and from lot to lot. Even the forest from which the wood is taken to make the charcoal is of importance. This means that it is all the more desirable to understand how it ignites, and perhaps to develop some means of testing the lots so that their pertinent parameters may be input into the ballistic models. But not only is the chemistry unknown, the starting materials, particularly those volatile ones, are not well identified or are often irreproducible. If one could better understand the mechanisms, one might be able to design a more ideal igniter, which is one which burns very, very rapidly before the propellant itself really starts to burn and one which ignites the propellant reliably.

There was concern about how the thermal wave moves from the igniter train into the propellant bed; why is it that heat from the propellant

does not overwhelm the heat from the igniter? If the thermal wave from the igniter energy passes through too quickly, less efficient propellant ignition will result. It was postulated that ideal ignition is when the rate of input energy is exactly the same as the rate of heat output from the propellant grain under the same conditions.

It was brought out that ignition occurs at low pressures, starting at 1 atm ambient and continuing only up to about 10 atm, while the propellant burning takes place at higher pressures, really getting going at 200 psi. This information sparked a sort of posturing discussion on the relative importance of different mechanisms. At these pressures, one might expect that chemistry is of some importance, and if black powder could be made to burn in a reproducible enough fashion to study it scientifically, perhaps some information could be gleaned here. But there is no actual evidence that chemistry is important for igniter materials, only a guess; maybe the fluid dynamics is all that is important. There is really no way to sort this out without some modeling that includes both the hydrodynamics and the chemistry, to assess the importance. One needs to design some experiments, in concert with the modelers, which can test some of the necessary assumptions. Even if one models, what is the beginning? One needs to know the solid phase decomposition products. In fact in both propellant and igniter combustion, the solid might control the whole thing, even in the case of the pressure dependence of ignition criteria, which suggests chemistry but can also be explained by alternative notions (discussed in more detail later).

There are many pieces which make up the overall view of propellant burning which are considered "chemistry" or "physics", and there are a large number of instances within the propellant community (and ballistics as a whole) in which the current thinking is divided into the "chemistry camp" and the "physics camp". The championing of a particular view can lead to a (hopefully subconscious) designing of experiments which exclude the influence of the other. But the chemistry and the physics interact with one another, no matter what the parametric-fitted type models imply. If one attempts to attain a real understanding of what's going on, this fact must be recognized and dealt with in an unbiased combining of all the component parts.

It was suggested that an overview of the modeling efforts and experimental measurements of ignition processes would be useful, particularly for those scientists engaged in more fundamental research into subprocesses and their mechanisms. No offers to put together such a review were made, and it appeared to be an appropriate time for Caveny to begin his presentation of actual observations of propellant ignition and combustion.

Caveny's talk gave an excellent feel for the problems involved in actual measurements on propellants by means of a brief review of time scales, methods of ignition, diagnostic techniques, and movies of igniting propellants. The mechanisms of handling such materials is non-trivial,

and the burning takes place on very rapid time scales. Thus fairly sophisticated techniques are necessary for relatively crude measurements (crude by the standards of the type of carefully conceived and controlled experiments more familiar to most of the participants). Nonetheless those data which do exist form the final "proof-of-the-pudding" in the testing of viable theories and mechanisms. Even if the details of the process are not evident in these measurements, some important aspects needed to formulate ideas are there.

Caveny described the several methods used to achieve rapid ignition, noting that radiative ignition (more conducive to lab experiments) is not the same as convective ignition (the likely mechanisms for actual propellants). His listing of the methods is included in Appendix B. He also described the techniques used to study the ignition processes, a listing of which is also in Appendix B. The methods there are self-explanatory, except perhaps for the term "ignition" under "global". By this it is meant that one uses the actual onset of ignition itself as a measurement to study the processes; obviously in an engineering sense this is useful in developing a picture of various dependencies of ignition. On the other hand, this is not necessarily cleanly definable either in experiments or in the models which are used to describe them. It is important that the criteria (in a mathematical sense, if possible) used to define the onset of ignition be spelled out. One would in this sense like to relate something relatively accessible and experimentally observable to something easily definable in the theoretical treatments with as little ambiguity as possible. This is not by any means a trivial undertaking, particularly given the necessary assumptions and simplifications in the models.

After concluding that at least an intuitive feel for what is meant by "ignition" should suffice for this discussion, Caveny described some actual measurements. He showed that ignition delay depended on energy flux, and that there was a definite flame-developing time, noting that optimum ignition is not the hottest ignition. These graphical representations of regions in which various processes (no ignition, extinction, self-sustaining ignition, etc.) take place vs time and heat flux gave some feel for the development of ignition but were not discussed by the participants in much detail. Again, though, they underscore the need for defining what one is measuring if one states that ignition has or has not occurred.

After it was noted that some of the results on Caveny's schematic plots could be considered to show that chemistry is important, but also could be explained without invoking gas phase chemistry, a discussion of the importance of chemistry ensued. Models of the kind of data which Caveny takes are predominantly fluid mechanical, in which the chemistry is included in a global fashion. That is, all of the chemistry is condensed into a single heat release rate which is then used in the hydrodynamic equation involving energy conservation. In some of the models, the heat release rate is a (sometimes floating parameter) single number;

in others an Arrhenius-style reaction description is used. In a very limited number of recent cases, real (multireaction) chemistry using independently determined rate data is combined with the hydrodynamics in a total model. These models must, on the other hand, deal with substantially simpler systems than those encountered in actual propellant burning due to the massive computational complexity. Simple flames and one example of an ignition process are all the combustion systems which have been treated in this manner to date.

Putting together such a model involves a need of determining the products formed in decomposition and carrying out independent kinetics experiments with those molecules. This would home in on the chemistry under conditions where perhaps some of the complications due to fluid dynamics could be ignored or at least handled with confidence. One possible such experiment would be to run a reaction (or actually a network of reactions, hopefully a sensibly small one) within a shock tube under conditions close to those of ignition. Then the reaction would be quenched (maybe by an end wall) just short of ignition, and one could analyze the product gases.

Certainly such work would help fix the chemistry, but is that where the knowledge is needed? We do know a lot about gas phase kinetics, but how much is known about general mechanisms of solid decomposition and, in particular, propellant solids? For example, even after the propellant decomposes, forming radicals in the gas phase above the surface, how do those (probably free radical) molecules in turn attack the solid and promote further reaction? (This could lead to some diffusion control especially in the case of composite propellants). Not much is known about such reactions. One means of inquiring into their phenomena is through decomposition and/or burning of actual propellant samples and measurement of the product gases. Work of this kind is being done using as the measuring techniques both gas chromatography and, under low pressures as well as high, molecular beam mass spectroscopy. In the latter experiments, results can be obtained at low enough pressure that secondary reactions among the nascent products do not occur before those products enter the sampling head. It is found that a great variety of products are formed from HMX and RDX, including several which cannot be readily explained by the propellant molecules simply breaking apart. Two findings of this work are noteworthy. Both types of experiments (gas chromatography and mass spectroscopy) show no differences with heating rate, implying that the same mechanisms (chemical) are going on and that they are not changed by the rate of heat transfer. Secondly, a major nascent product from HMX is N_2O , which indicates that some chemistry has taken place somewhere (Figure 1 shows the HMX and RDX molecules for reference), since formation of this species involves either a rearrangement of atoms within the molecule or some bimolecular reaction.

Caveny then presented data showing that the time it takes to heat a propellant surface until self-sustaining ignition is achieved depends on the thickness of the gasified layer above the surface, and is

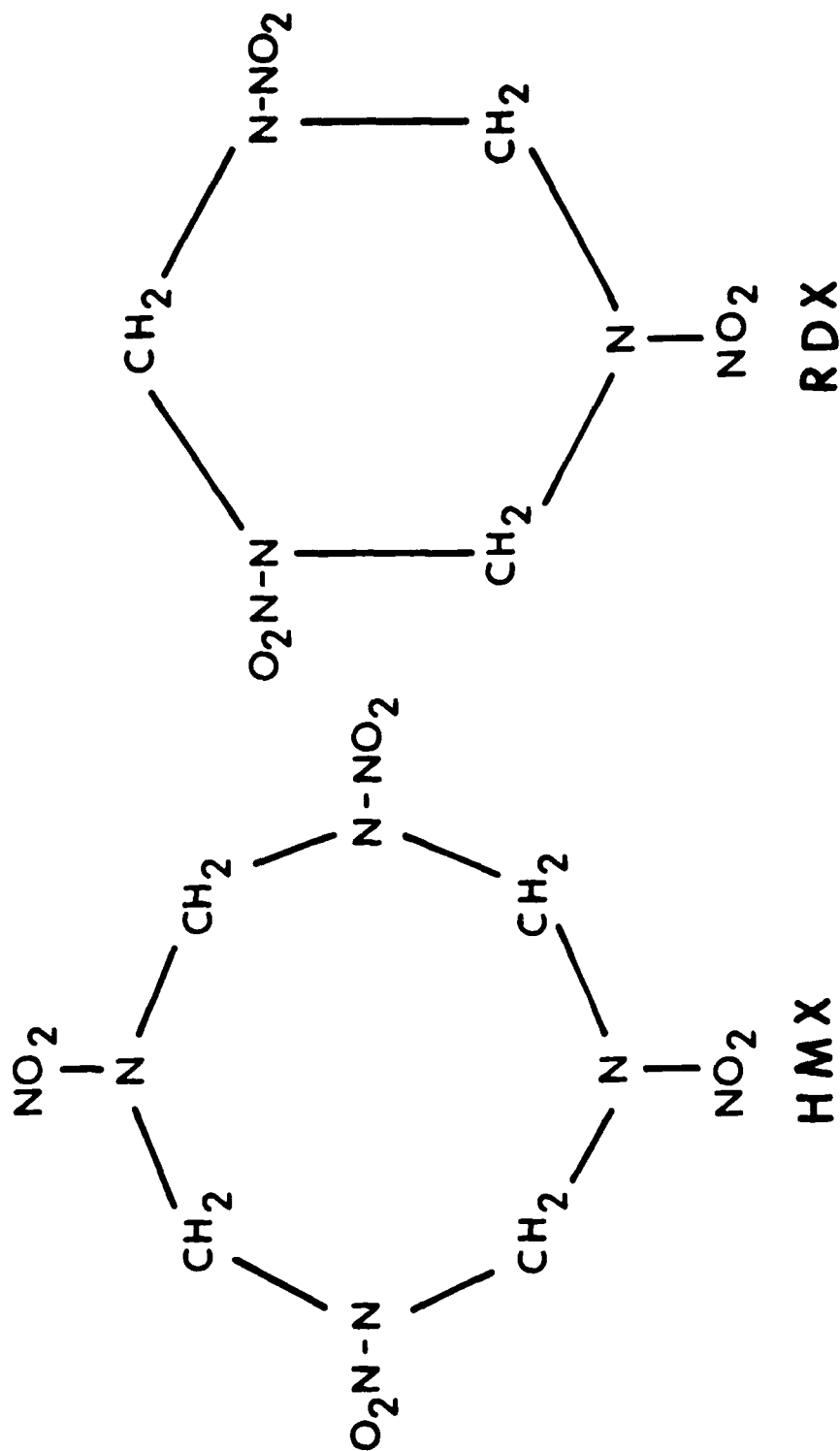


Fig. 1. The molecular structure of the two premier nitrairine propellants.

pressure dependent. This is for experiments in which radiation is the igniting source. From this, one might think that gas surface reactions should be immediately implicated. However, there exist other recent studies which show that, for radiative ignition, the gases above the surface can also absorb the radiation, augmenting the reaction. This is true at least for cellulose, through it could be the case for the propellants as well. As further gasification occurs, the gas-phase light absorption could increase in net efficiency.

Motion pictures were shown by Caveny showing both radiative ignition of a propellant and convective ignition within a shock tunnel. The former is a most "mechanically complex" process; prior to ignition, a cloud of gas-like material is evolved, even when an ignition threshold is not attained. When the surface reaches self-sustaining burning, material in bits and pieces is ejected and thrown off, and small pockets occur in the surface. In the convective ignition within a shock tunnel filled with O₂, there is a competition between the reactions occurring and the flow velocity. This determines the point on the solid which ignites first, and flow calculations can be correlated with the observations. The occurrence of ignition is highly dependent on O₂ concentration, when mixtures are used.

The discussion returned to the question of radiative ignition and the influence of gases above the surface of the propellant itself. While this is important, the internal temperature of the gases above the surface could have an influence. The temperature of the surface itself is difficult to measure, so it is not really known whether the lower temperature decomposition studies are fully pertinent to ignitive decomposition. Another question related to the surface temperature is whether the propellant surface attains a high enough temperature that a change in its properties occurs? This could be phase change, and propellant molecules such as HMX have several different crystalline phases which may behave differently.

Another possibility is a chemical one, that after some decomposition has occurred, the surface is not just "pure propellant" but also contains some product species, some of which are found in thermal decomposition studies to be a solid or tarry residue. Some evidence for the latter is that the rate of gasification has in some studies been found to depend not just on the temperature as such, but also on the thermal history of the sample. This kind of behavior could only be the case if the surface composition were also a function of time, that is, that it changed during the decomposition.

It remains true that a good deal of our knowledge of what is going on in ignition processes is derived from studies of radiative ignition, whereas it was pointed out the convective ignition is the likely mode in an actual propellant case. These latter studies are tough to carry out, though a couple of projects are now underway to look at the process. It is the radiative ignition results which are input into many of the

models, although the mechanisms may be quite different. For example, it is possible that much of the chemistry in the gas phase is controlled by diffusion process, not by chemical rates, in the case of convective ignition; whereas the converse is likely in the radiative ignition studies.

III. THURSDAY AFTERNOON

The afternoon session began with a talk by Benson, who placed detailed modeling of complex gas phase reactions in historical perspective. He introduced his comments with the statement that "Nature has never been so kind as to let us do something simple". He pointed out that in the past it was necessary to use global rates because high speed computers were not available that could handle all the reactions. Also, rate constants were not available for many of the important elementary reactions. These are no longer obstacles. There are, in fact, many situations where global kinetics simply do not work. Benson mentioned catalysis and inhibition as examples where global kinetics might be expected to fail. He illustrated this by showing modeling calculations for a reaction involving inhibition by HBr. In the many-step reaction model for this system, all the reactions for the uninhibited reaction needed to be explicitly included in order to correctly predict the effects of the added inhibitor. The explosion limits of H_2/O_2 were described, as well as the phenomenon of "cool flame" ignition in propane/oxygen mixtures. (This system can react in any of four ways, depending on the temperature and pressure: explosively, with a blue flame, with a "cool flame", or with slow reaction.) The various limits for these systems can now be explained and predicted on the basis of differences in the chemical mechanisms under different conditions. It therefore appears that the ignition limits for homogeneous systems are now fairly well understood. Benson felt that the main impediment to modeling the fundamental process of energetic material combustion was not a lack of ability to do the modeling, but rather a lack of information as to what reactions take place. "There has been very little fundamental research in explosives to look at mechanisms in the last 20 years". Most studies have not gone beyond measuring the kinetics of the first step of the solid phase decomposition. The mechanisms of decomposition and oxidation of many relatively small molecules (hydrazine, for example) have not yet been determined. Benson concluded by expressing the opinion that the ignition and combustion mechanisms of propellants and explosives are probably sufficiently complex that they will not be successfully modeled with the kind of simple, global rate schemes used in the past.

Benson's comments led to a discussion of what is known about the gas phase reactions of propellants and other important combustion systems. It was pointed out that there have to date been no successful quantitative measurements of species concentration profiles for the flame zone of burning solid propellants. The experimental difficulties involved in making such measurements were briefly discussed. For burning propellants, these include: a) the extremely thin reaction zone (a few hundred

microns or less even at modest pressures), coupled with surface irregularity, makes optical probing difficult, b) the high content of particulate matter in the more distant, hotter flame zone, which makes conventional absorption and emission spectroscopy there difficult, and c) the transient nature of the process necessitates rapid measurement techniques. (Ignition is transient in the true sense of the term. However, it might be much easier to probe the larger and cooler "cloud" of reacting gases present prior to flame development.)

In view of this situation, the question was then raised: "What are the chemical problems in propellants that can and should be studied?" The answer, voiced by several of the participants, was that we need to study the chemistry in simpler reaction systems that are more controllable, cleaner, and not plagued by the thin reaction zone of the solid propellants themselves. At the present time, we can best determine which reactions might be important in the flames of solid propellants by looking at the thermal decomposition products, which for most propellants have been extensively studied. By separately measuring the reaction intermediates, and determining the mechanisms, of these simpler sub-reactions with a variety of techniques (eg. shock tube, flow systems, diagnostics on burner flames, etc.) it should be possible to construct a reasonable model for the gas phase flame zone for a given type of propellant.

For example, it is widely believed that the primary flame zones of both nitrate ester and nitramine propellants are dominated by the reaction of formaldehyde (HCHO) with nitrogen oxides (NO_2 or N_2O). Burner flames of these gases could be set up and studied. Diagnostic techniques would be used to identify the important species and reactions in the flames. Calculations with newly-developed flame codes would confirm the mechanisms and kinetic data, and indicate the importance of non-chemical processes such as diffusion and heat conduction. Finally, the model could be used to predict the primary flame zone width and other measurable properties, given the propellant surface temperature and the composition of the gases leaving the surface.

One of the participants expressed the feeling that global representations of complex chemical systems will always be necessary for practical modeling of most complex combustion systems. Such global representations need not be single step -- there can be two, three, or more steps, whatever is needed to successfully model the reaction. Detailed modeling, however, is done first, and used as the basis for construction of the multistep global model. This kind of simplified chemical scheme will be useful for modeling complex end-item systems that involve so many difficult-to-model physical processes that the inclusion of a complete reaction scheme becomes impractical for computational reasons. It was pointed out by another participant, however, that even if the results of a chemistry-only experiment are well defined, it may nevertheless fail in certain applications -- for example, if diffusion or some other non-chemical process significantly changes the local concentration of some reaction intermediate not explicitly represented in the global model.

The discussion then shifted to the solid phase reactions of propellants and explosives. The question was asked: "Can we do better than just determining the kinetics of the first decomposition step in the solid phase? Unexpectedly, this led to quite a lively and lengthy discussion. One participant insisted that multi-step chemistry does not occur in the condensed phase: that the initial decomposition-bond breaking reaction at the propellant surface constitutes the entire condensed phase reaction, since molecules in the solid phase would have to be able to move around in order to be able to undergo subsequent secondary bimolecular reactions. ("These molecules are not gymnasts, are they?") Another participant, on the other hand, mentioned experimental evidence indicating that, at least for certain propellants, quite an extensive reaction takes place in the condensed phase. This led to some speculation concerning the possible mechanism(s) for mobility in condensed phases (diffusion, reaction in gas pockets, etc.), and brought up the problem of how one could model a multi-step condensed phase reaction even if the chemical mechanisms were known. Most present saw this as a very difficult problem, although a couple of people expressed the opinion that the theoretical methods are probably available for doing so if the chemical mechanism and the mobility process were both known. One person brought up another possibility: that many of these reactions are not condensed phase reactions at all, but rather surface reactions.

Solid phase and surface reactions are not presently being directly probed. Most of our information about these processes comes from analysis of decomposition gases after they have left the vicinity of the propellant, and it is not possible to determine from such measurements where the reactions took place. New diagnostic techniques will have to be employed if these questions are to be answered.

This discussion was followed by the talk by Golden, who described his research into the gas phase unimolecular decomposition of molecules used as explosives (TNT, HMX, RDX). The purpose of this research is to establish more reliable rate constants than have been derived from previous studies with the solids and liquids. His research is carried out using the very-low-pressure-pyrolysis technique. In this technique, very low pressures (typically a few microns or less) of the gas are contained in a heated chamber. The pressure is sufficiently low that gas phase collisions do not occur, only collisions with the walls of the chamber. The unimolecular reaction is assumed not to take place on the wall, however, although subsequent bimolecular reactions of the decomposition products may be heterogeneous in some cases. Despite the low pressure, the unimolecular decomposition is probably still in the first order pressure-independent region, due to the large number of vibrational degrees of freedom in a molecule of such size. The kinetics and products of the unimolecular decomposition are measured by continuous sampling of the gases through a small orifice; the size of the orifice determines the residence time of the gas in the heated chamber.

For experiments with HMX, the ratio of N_2O to NO_2 is higher for smaller orifice sizes (longer residence times). This suggests the N_2O is a secondary rather than, as often assumed, a primary product of the HMX decomposition. Results for both HMX and dimethyl nitramine suggested that molecular elimination of nitrous acid ($HONO$) may be a homogeneous process. Golden also talked about transition state theory and its value in providing theoretical estimates of rate constants or in checking the validity of experimentally measured rate parameters.

At the conclusion of this talk, Golden was asked to make some rate constant comparisons for HMX decomposition from the solid, liquid and gas phases, the rate constants being obtained from different sources. Although they exhibited widely varying activation energies and preexponential factors, it looked as if the rate constants were all of about the same order of magnitude if calculated for the same temperature. There arose some discussion concerning why this should be the case. One interpretation is that for HMX there is only a single reaction in the condensed phase, or, if there is more than one, only one is rate determining and there is no chain reaction. An autocatalytic mechanism, as often proposed for HMX, would also be expected to result in much higher rate constants for the solid -- a trend that was not at all apparent in the rate constants being compared. The value of rate constants of reactions in different phases became apparent. There was some discussion concerning how such rate measurements relate to various problems of real propellant ignition and combustion, and about other similar experiments that might be of value.

IV. FRIDAY MORNING

One of the participants described recent experiments which have been carried out on the thermal decomposition of HMX. The means of doing so was to put the HMX in a boat within a quartz capillary and to flow heated helium over the sample, then analyze the resulting products using gas chromatography or wet chemistry. The temperature of the entire system could be varied between 300 and 1000°C. What is found is a variety of product, generally stable molecules but whose relative yield varies a great deal with temperature. Most surprising was the fact that as the temperature was increased, the yield of HCN increased. These data can be interpreted to say that the thermal decomposition products vary as a function of temperature, meaning that the thermal decomposition studies carried out near the melting point of propellants are not necessarily valid for the surface temperatures of burning propellants. On the other hand, it can be argued that the product distribution in these experiments reflects not the nascent thermal decomposition products but rather the results of secondary reactions within the flow system, prior to the analysis. While the mass spectroscopy results mentioned on Thursday morning would seem to obviate that problem, there is some question in those experiments as to whether the means of initiating the decomposition, often laser pyrolysis, allows the propellant molecules to actually attain any kind of thermalization before they decompose, so that the product distribution may then not be pertinent to the presumed temperature.

One question, among several, which can be raised in this context concerns the several phases of molecules like HMX. It is known that in the region of the melting point there are phase changes, but during an actual propellant decomposition process (under "real" conditions), is the phase of the substance controlled by the thermo-chemistry, or do the kinetics of the phase changes make a difference? That is, the heating of the surface in the convective ignition process may be so rapid that the phase-change kinetics are limiting. A question as to the state of knowledge of the kinetics of phase change went generally unanswered. It was suggested, however, that the real limiting parameter was that of heat flow within the solid, which is slower than the other events. Thermal conductivities are important to all the models of ignition, but they are measured not at the temperatures pertinent to ignition, rather they are known at room temperature and extrapolated to the assumed surface temperatures. Even not counting the problem of insufficient knowledge for confident extrapolation, there then also exists the worrisome difficulty that if a phase change does occur, how can one extrapolate the thermal conductivities?

This returned the discussion to further consideration of the chemistry within the condensed phase. It was asked, do we know or not know whether there exist sub-surface reactions? Cannot an experiment be designed which says yes or no? The argument was advanced that only negligible reaction should take place within the solid, that all the action is in the liquid layer above the solid and in contact with the gas. Would it be possible to model these aspects of the problem and assess the relative importance of liquid and solid reactions?

These considerations of the regimes in which the pertinent chemistry was occurring, together with the recognition that modeling was necessary to put it together, formed an appropriate introduction for Kooker's presentation. He has been carrying out a complete model of the ignition process in which O_3 is brought into contact with a heated surface and, in time, ignites (or does not, depending on conditions) according to the reaction decomposing through the O atom intermediate to O_2 . The detailed chemistry is included as well as the diffusion coefficients for the species.

Again, a key point here is in the definition of what is meant by ignition. Within the model, it is relatively easy to discern, since it means that the reaction is self-sustaining, i.e., does not extinguish. That is not so easy to relate to experiment, however, unless one is directly measuring the same pressure vs time kind of observables.

For such models, the usual output is the time to ignition. This is certainly reasonable from the point of view of the user of the output of these models (typically an interior ballistician) but doesn't say much about the model. Kooker showed that three quite diverse models, based on different theoretical frameworks, yielded about the same answer to the ignition time. Consequently the value of this quantity, regardless

of its utility, cannot be used to speak to the validity of the details of any of the models.

Kooker's model (which includes the detailed chemistry and individual diffusion coefficients for each of the three species present) raised the question as to whether the inclusion of different diffusion coefficients really makes a difference, but the full model has been running for too short a time for him to know. A different model (carried out by another investigator) of the ozone flame on a steady state basis does show that one must include the detailed transport properties in order to correctly calculate the flame speed for a range of O_3/O_2 concentrations, when the correct and detailed independent kinetics are included.

The fact that the ignition time is insensitive to the model suggests that one need not be especially careful and detailed if this kind of gross parameter is all that is desired, within the range of the parameters covered in the experimental data used for fitting the model. However, one would certainly like to have the model placed on a firm microscopic basis. This is obviously difficult for a large reaction scheme if one must include separate diffusion coefficients for each of the species in the mixture. Development of a sound model, but with some simpler approximations for all the transport coefficients, can be accomplished perhaps with a great deal of data on the gross parameter, such as ignition time vs heat flux.

The general question, "How important is the chemistry?", was asked of Kooker concerning his model. The level of importance, and how much must be included in a detailed way, depends on how predictive one desires the model to be. The example of Benson's description of the HBr inhibition was referred to; clearly there a global chemistry approach does not work, and the real chemistry cannot be approximated by one step or some one rate-controlling reaction. It was suggested that one might conclude that unless the detailed chemistry is included, one might never be able to predict what is going on with confidence (as opposed to merely obtaining a fit).

The problem with full inclusion of the detailed chemistry -- apart from worries about lack of knowledge of the rate constants -- is that it is an expensive process. For Kooker's transient, time dependent model, he spends about a quarter of the time on the flow dynamics part and about three quarters on the chemistry. And this is about the simplest combustion reaction network around. Other modelers performing flame calculations in a similar spirit (there are few) find also that the bulk of the computer time is spent on the chemistry.

One hopeful approach may be to calculate the chemistry first, separately. This could then be distilled to be put into the flow dynamics codes, perhaps by picking out the one or few reactions which are controlling under the particular conditions present. Another possibility would be to calculate the chemistry for the pertinent conditions and reduce

the whole network to an artificial heat release rate for that given pressure and temperature. Moving to another P and T, the chemistry code (based on sound microscopic kinetics) could be again run, yielding another value of dQ/dt to be put into the hydrodynamics.

Although one cannot generalize yet, this cannot be done for the small-system models such as Kooker's ozone calculations. Here the chemistry and the transport aspects are intimately linked; it is not a question of one driving the other or vice versa. Thus it has to be done all at once. Perhaps a larger system would be "more statistical" such that some shortcut methods would be not only useful but also of some validity.

This notion of a hierarchy of models, of distilling the results of one and using that as input to the next, continues up the line toward applications, at least as far as propellants are concerned. The interior ballistician wants to know, for his models designing barrel and projectile shapes, etc., the ignition time. He doesn't care about the details and they are of no importance to the results he calculates.

One point that modelers should keep in mind is that they should not attempt to put together the whole thing right at the beginning; it is worthwhile to start with some questions and help to guide the way to the approach which best describes the real system.

Considering the necessary complexity of the models, the question was asked, "Are the modelers in fantasy land, or is there actual hope of being able to develop a predictive model for a real system, based on sound microscopic ideas?" It was replied that use of a model has enabled prediction of nitrocellulose ignition times using a model of nitrocellulose decomposition. But that was done using data from radiative ignition, and it was only a feeling that convective ignition could correctly be incorporated.

"You can't model the entire universe at once; it has to be divided up somewhat". One should aim a model to concentrate on one or two features which are important for the problem at hand. In fact, particular problems may require particular models tailored to what is needed. Some not very fruitful attempts have been made at putting together a unified model which explains all. The Soviet workers connect steady state burning with surface temperature and then deduce everything else they need from that. Not considering that the surface temperature is itself an experimentally elusive quality, they give no details of their models so that it is impossible to really assess what, if anything, they've really accomplished.

But the data and the knowledge on the detailed processes are so scarce, in any event, that any information would be useful. It has already been pointed out that there exist to date no measurements of species profiles in a propellant flame, or even a "simulated" propellant flame. If one can put together a gas phase model which predicts real

observables and can really be related to experiment, then it should be pursued. One can certainly learn something from such work, even if all the problems are not solved and the "useful" parameters fully deduced. It should provide some insights and probably some usable information.

One approach is simply to put everything in the model, and then let the experiments say which processes are unimportant and can be removed. That may or may not vary with conditions; one view was that it was doubtful that the gas phase was the most important at one time and the surface important at another. Another felt that neither should be thrown away, but a third furnished a reminder that, from the more applied viewpoint, the model should be tailored to what is needed.

One question is where to start with in the gas phase chemistry. Is it obvious that one should do formaldehyde -- nitrogen oxides reactions in order to get useful information? Do they need to be studied separately? Maybe there is no $\text{CH}_2\text{O}-\text{N}_2\text{O}$ reaction at these temperatures.

The temperature of interest to ignition is, at the low end, 600-700°K and at the high end, 1500°K. This is between the room temperature range that exists for many rate measurements and mechanisms and the shock tube results that provide information typically at higher temperatures. There is actually little on formaldehyde chemistry in this region. For example, decomposition of CH_2O is likely important, but extrapolation of the high temperature results downward doesn't make sense. There is probably a different mechanism in this temperature range.

It was pointed out that something the propellant community could really use was measurements of reaction rates within this range. But one doesn't always have to measure them; in many cases estimation procedures based on transition state theory provide adequately accurate estimates. The models often do not need all of the rate constants to be of uniformly high accuracy, but typically only a few need to be known well, and the rest can contain larger degrees of error. Consequently the estimation procedures should be quite useful. In addition, this points to why one should just get in and model and try to get out some actually measureable quantities.

What should be done in this connection is the following. Decompose the propellant and measure the products. Then run a flame using these as starting materials, make some detailed measurements, and set up a model of this flame. Here one could isolate the chemistry. A propellant flame itself is too complicated and would be experimentally untractable, due to the high pressures involved. Rather, do something like starting with a vessel of heated formaldehyde and mix it with some oxides of nitrogen.

One of the participants soberly reminded the group that somewhere in here the condensed-phase part of the problem had again been forgotten. Most of those present were more comfortable, both conceptually and in

considering possible experiments, with the gas-phase. But this zeal should not be allowed to draw everyone away from the whole problem: "Don't shirk the condensed phase just because it is messy." In fact, even when the gas phase is clearly important, the solid takes a lot of time to heat and get going. If one is really interested in the ignition time, the solid aspects of the problem may be those most responsible for the ignition time of a solid propellant.

One participant expressed the concern that the condensed phase is very difficult to work in, particularly to make measurements. Should one measure things in the gas phase and try to tie them to what's going on in the condensed phase? Here the modeling would be a necessary part of the attack. But another replied that one could make useful measurements just by working in the liquid itself and looking at the products; from this the rates can be obtained.

One participant returned the discussion to gas phase considerations, pointing out that in actual propellants there may be important reactions which are not usually considered by those concerned with steady-state burning as opposed to transient events. For example, in the HF laser, one rarely considers the reaction of $H_2 + F_2$ going to $HF + H + F$. Perhaps the wrong reactions are really being studied in the laboratory measurements of rates. However, if one is building a large-network model, it isn't much extra work to add in all such possibilities. It was then argued that the reaction used as an example had too large an activation energy to be of importance, that $M + F_2$ going to $M + F + F$ was a better first step. Using estimation procedures, one can sort a lot of these things out. A great deal of the pertinent chemistry can be explained well by looking seriously at the ordinary reactions; we should not devote a lot of time to consideration of peculiar reactions no matter how interesting they may appear.

V. WRITTEN COMMENTS FROM PARTICIPANTS

Toward the end of the meeting, the participants were asked to split up into small groups of three or four persons each and to discuss and put on paper their feelings and thoughts about the discussions that had taken place. No specific instructions were given as to whether these comments should be assessments of our current understanding of ignition processes or suggestions for future research. The participants were free, for that matter, to express their feelings about what had been said at the meeting or about the success (or shortcomings) of the meeting. In composing these groups, an attempt was made to obtain a mix of the represented research areas.

In many cases, these groups made suggestions for research that they felt would further our understanding of the fundamental processes involved in ignition, with indications of priorities as perceived by the members of that particular group. Some comments were assessments of our current

status in a number of areas. This indicated how the participants viewed the relationship between experimental research and theoretical modeling, or suggested areas where information might profitably be provided to the research community so that they would have a feeling for what experiments might be profitably attacked.

The written comments that each of these subgroups produced are shown on the following pages. They have been edited only where necessary in order to make the statements more readable, or in certain cases for clarification of the intent of the statement.

A. Working Group Comments - Subgroup #1

1. Recommended priorities.

a. Develop and explore the "pure gas phase" kinetics of the decomposition products of a) HMX and RDX, b) nitrate esters.

b. From the above, determine a) which elementary reactions are important, b) what rate constants must be experimentally determined.

c. The propellant community should define the temperature/pressure ranges relevant to ignition processes, so that experimentalists can perform experiments on model systems under conditions corresponding to ignition of real propellants.

d. Experiments should be performed on the possible heterogeneous reactions between the gaseous propellant decomposition products and the hot propellant surfaces.

e. Experiments should be performed to determine, to the extent possible, the gases evolved from laser-heated nitramines and nitrate esters a) into a vacuum b) as a plume into an atmosphere of inert gas, and c) into reactive gases. This should be done, if possible, both with sampling probes and using time-resolved spectroscopy.

f. For researchers not familiar with the solid propellant literature, the following information, in order of DOD interest, would be most valuable: a) propellant types and composition, b) types of ignition sources, and c) bibliography of past and in-progress ignition modeling efforts.

g. Meditate productively on the results of a through e.

B. Working Group Comments - Subgroup #2

1. To further our understanding of fundamental processes:

a. For gas phase reactions make use of:

- (1) optical techniques to identify intermediate species
- (2) shock tube chemical kinetic measurements
- (3) mass spectroscopy of rapidly pyrolyzed samples
- (4) laser diagnostics, (e.g. tunable lasers, ir to uv), which can provide microsecond time resolution
- (5) stirred reactor experiments - compare to shock tube and flow reactor results

b. For solid phase reactions: Analyze melt layer relics for entrained intermediate products.

c. In general, if feasible and promising:

(1) Attempt to transfer knowledge from the field of detonation to that of ignition.

(2) Consider in each experiment the potential advantages to be gained by isotopically tagging the components of the molecule.

(3) Perform experiments on simple, or model systems if the results will be simpler to interpret on a fundamental basis than those on the propellant itself.

2. For applied developmental efforts:

a. Derive simple ignition criteria from experimental results (e.g. critical surface temperature or simple temperature-time relationship). Simple relationships may be possible if in the vicinity of "runaway" large variations in applied energy cause only small differences in ignition time compared to those produced by uncertainties in such properties as thermal conductivity.

b. As a measure of success, we should attempt to explain, at least qualitatively, the important ignition difference between the major propellant types (single, double and triple base, AP and HMX composite).

c. A detailed knowledge of kinetics is vital to the pursuit of methods to a) accelerate the combustion process, i.e., control the burning rate, and b) inhibit ignition, i.e. make low vulnerability ammunition.

d. More knowledge of convective ignition is essential. Since this is a flow process, the reaction time of the gas phase process will be needed to obtain any kind of correlation.

C. Working Group Comments - Subgroup #3

1. Requirements Related to Modeling:

a. Continued development of semi-empirical models to further develop capability of handling real situations more efficiently.

b. Attempts to develop simplified models that apply only to particular subprocess but that treat these sub-processes in a more believable way.

c. Information on chemical mechanisms and rates, both for use in models and for understanding the behavior of propellants. This is especially needed in nitrogen-containing systems, where little information is currently available.

(1) Gas phase chemical studies, since gas phase processes are known to be important for combustion and are probably critical to the ignition process as well.

(2) Chemical kinetic parameters for the condensed phase reactions, which are probably important for most propellants. Also, ways of representing and modeling complex condensed phase processes are required.

d. Testing of the predictions of models (that use chemical kinetics derived from fundamental studies) against the results of laboratory experiments should be idealized, easily interpreted experiments on simple systems rather than such complex processes as gun charge ignition.

e. Iteration between the basic data, the models, and the experimental measurements in order to improve the models and the data base.

D. Working Group Comments - Subgroup #4

1. Comments:

a. Ignition is the result of competition among many rate processes. These can be initially separated into chemical and physical processes for the purpose of discussion, always remembering, however, that they are strongly coupled.

b. If all the important processes were gas phase, the physical processes would be well understood and the chemical processes would or could be known. Under these conditions, the major future efforts would probably be: a) model development, and b) measurement of some specifically needed rate constants and species concentrations. However, an important question is the relative importance of the other phases. Here, very little is known. Future efforts should include experiments and modeling:

(1) Experiments should be designed to get even a crude understanding of the nature and extent of processes in the condensed phases and on surfaces. If condensed phase processes are important, it will be necessary to get more detailed mechanistic and rate information. If surfaces are important, it will be necessary to apply surface diagnostic techniques that have not yet been used with propellants.

(2) In real ignition systems where convective ignition is important, a two dimensional model will have to be developed and some thought will have to be given to how experiments can be compared to the predictions of the model.

2. Conclusions.

Ignition is a very complex process. The chemistry of ignition is known only very superficially. None of the modern techniques of analysis have yet been successfully used to analyze the vapor and condensed phase reactions of propellant ignition and combustion. Modelers and chemical kineticists need to communicate better with each other, as well as with the people in the field who have the real needs and problems.

VI. A COMMENT

In retrospect, it may be properly asked whether a workshop held in this format is of any value to anyone save the participants themselves. In this report we have attempted to faithfully record what was actually discussed in chronological fashion, so as to provide the kind of information an invisible observer would have gone away with. In this context we refrain from making any overall summary, drawing conclusions of our own concerning the content, or engaging in the customary practice of making recommendations about the subject matter.

One noticeable difference between this workshop and the usual scheduled-presentation format was obviously the planned free discussion. In our opinion, the difference between a workshop and a meeting should be that workshop papers are considered interruptible in principle and are interrupted in practice, for extended periods of group discussion. This may actually be accomplished more easily by collecting scientists from at least somewhat diverse disciplines, instead of assembling only the experts in a given narrow specialty. Certainly the participants in this workshop, well recognized in their areas, were not at all bashful in asking simple and elementary questions in an attempt to understand what was being discussed. It is our own experience that we seldom, if ever, fail to gain in our own understanding of our own specialty when forced to consider and discuss some of the simpler foundations of what we are doing. It may even be useful, when holding workshops in the more usual format, to "seed" the audience with a few persons who can provide such stimulus. One should neglect neither the forest nor the trees.

Finally, the fewer the attendees and the more open the discussion, the sooner a transcript of the meeting needs to be published. Again in retrospect, we could have improved the usefulness of this workshop to others if we had firmly established, before the workshop, the details of the mechanism of writing, editing, reviewing, and publishing this report. We apologize for any inconvenience we may have caused.

ACKNOWLEDGMENTS

We thank Dr. David Squire of the Army Research Office for his own encouragement and efforts which made this workshop a possibility, and Ms. Betsy Laurie of the Ballistic Research Laboratory for her handling of the local administrative details.

APPENDIX A.

WORKSHOP CORRESPONDENCE

This letter, reproduced verbatim, was sent to each of the participants on 6 June 1978, following earlier telephone contact. It is included here to describe the spirit in which the workshop was organized.

DRDAR-BLP

6 June 1978

Dear Participant:

This letter is to remind you of the objectives and spirit of the workshop on propellant ignition to be held at the BRL on 15-16 June, and to provide some directions as to the location of the meeting and motel.

As we have discussed with most of you by phone, we are attempting to put together a workshop of a rather different type than is usually done. We wish to address the question of the mechanisms of propellant combustion, and the role, if any, played by gas phase chemistry. Little exists in the way of a full understanding of this process. The workshop participants are drawn from several fields: actual ignition measurements, thermal decomposition studies, chemical kinetics, and modeling. We wish to explore the relationship among these (often diverse) fields of inquiry.

We plan to have one speaker from each of these areas, presenting a semi-review talk of a hopefully provocative nature. The rest of the workshop will be devoted to discussion, moderated by ourselves, and with the intention of providing ideas concerning a microscopic description of the ignition process, and connection of results and concepts from the several fields of expertise represented. Rather than attempt to attain definite conclusions, we expect that simply the posing of questions will be an important part of the output of the workshop. Identification of promising experiments or calculations will be very useful.

We are hoping that each of you will be prepared to fully exercise your imagination and participate in some speculative discussion. There will be no format to the meeting except for the four scheduled speakers, and you should bring any slides, viewgraphs, etc., which you feel could be useful in the discussion section.

The meeting will be closed to any one but the invited participants, by which means we hope to foster free discussions. Also, we plan to publish the ideas discussed as a BRL report, though with no attribution of individual comments to individual speakers.

This format of a workshop is something of an experiment. We hope that though it some genuinely imaginative and worthwhile ideas, especially crossing fields of research, can emerge. Doing so will require earnest participation on your part -- in short, we hope that as moderators we'll have little to do!

The meeting will be held in Bldg 394 at the BRL, to begin at 8:30 a.m. on 15 June. You should come to the Visitor Control Center in Bldg 328 (see map) where you will be met. A dinner (open menu) Thursday will be held at the Colonel's Choice restaurant, with a social hour (cash bar) beginning at 7:00 p.m. We will collect \$3.00 at the start of the meeting to cover coffee and donuts at the workshop and hors d'oeuvres at the restaurant. A table has been set aside each day for lunch at the APG Officers' Club.

The only way to get to Aberdeen is by car; if you are flying you will need to rent a car. Get off I-95 at MD 22.

A couple of reprint articles are inclosed to provide some background on propellant ignition, particularly for those of you not working directly in this area.

Sincerely yours,

1 Incl
as

DAVID R. CROSLEY
Ignition and Combustion Branch
Propulsion Division

ROBERT A. FIFER
Ignition and Combustion Branch
Propulsion Division

APPENDIX B.

LISTING OF PROPELLANT MEASUREMENTS

Caveny's review of measurements on propellants included lists both of laboratory methods used to achieve ignition, and diagnostic methods used to discern whether or not ignition had occurred. These two lists, copied from his viewgraphs, form this appendix.

1. LABORATORY METHODS FOR ACHIEVING RAPID IGNITION

Conductive: Hot Plate/Wire (Solid-Solid)
Shock Tube End Wall (Gas-Solid)
Hot Particle or Hot Slag (Solid/Liquid-Solid)
Adiabatic Compressor (Gas-Solid)

Radiative: Lamps (Arc-Image)
Laser (Continuous Wave)
Laser (Pulse)

Convective: Flame/Torch
Shock Tunnel
Penetrative Ignition (Porous Beds)
Plasmas

Other: Hypergolic (Oxidizer-Solid)
Spark Discharge
Microwave
Molecular Excitation by Radiation
Friction

2. DIAGNOSTIC TECHNIQUES IN GENERAL USE

Global: Ignition

Visual: High-Speed Photographs
High-Speed Shadowgraphs and Schlieren

Detectors (Non-Intrusive): IR Detectors
Band Pass Filtered Photographs
Heat Flux Gauge Behind Specimen
Spectrographic

Detectors (Intrusive): Thermocouples
Fuse Wires
Gas Sampling

Relic Examination: Scanning Electron Microscopy
Surface Layer Chemical Analysis

Miscellaneous: Interrupted Ignition Sequence

APPENDIX C.

LIST OF QUESTIONS

One of the invited participants, Berge Goshgarian of the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base, California, was forced to cancel due to a last-minute conflict. He however did submit a list of questions which he thought might be useful to have considered at the workshop. While many of these are oriented toward specific and particular details pertinent to HMX and RDX themselves, as opposed to the more general tone often taken during the meeting, they nonetheless exhibit the kind of questions which one needs to know and which one hopes can be provided through a more fundamental understanding of the processes involved. The questions are included in this appendix taken verbatim from Goshgarian's list.

1. Is the HMX entering into the propellant combustion process the β - or δ - polymorph?
2. What is the latest on identification of initial HMX decomposition products and activation energy at one atmosphere and at high pressure?
3. Is there a pressure/surface temperature/burn-rate regime where condensed phase or other reactions predominate? Can a changeover from one type of reaction to another be predicted and measured?
4. How much do condensed phase reactions control burn-rate? How should these reactions be measured, e.g., DSC, MS, IR, etc?
5. If one must choose one parameter for conducting lab studies on propellant/ingredient decomposition and ignition, which would be the more desirable, low pressure (<1 atm), high pressure (>1000 psia), or high heating rate (>100°C/min)? By more desirable, I mean the parameter that will provide data useful in predicting rocket motor firing characteristics.
6. What type of burn-rate measuring device produces most representative data of propellant ignition/combustion characteristics at pressure to 3000 psia?
7. Must a particular burn-rate measuring device be chosen for a particular propellant formulation to obtain useful data for predicting rocket motor firing characteristics?
8. Has anyone conducted a detailed comparison of lab scale propellant/ingredient decomposition, ignition, and combustion data to burn-rate measuring and motor test data?

9. We will begin an in-house FY79 program to measure and compare burn-rate data with lab scale low and high pressure thermal decomposition data on propellants and ingredients obtained using DSC, MS, IR techniques. Any input on this or other subjects or comments by attendees will be appreciated.

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