AD-A204 136

OCUMENTATION PAGE

Form Approved
OMB No 0704-0188
Exp Date Jun 30, 1986

CATION
Unclassified

1b RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5 MONITORING ORGANIZATION REPORT NUMBER(S)

DTIC
ELECTE
10 FEB 1989
S D
E

6a. NAME OF PERFORMING ORGANIZATION
US Army Research Office

6b. OFFICE SYMBOL (If applicable)
SLCRO-CB

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (*City, State, and ZIP Code*)
Research Triangle Park, NC 27709-2211

7b. ADDRESS (*City, State, and ZIP Code*)

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

8b OFFICE SYMBOL (*If applicable*)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (*City, State, and ZIP Code*)

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO
61102		08	

11. TITLE (*Include Security Classification*)
(U) Nitramine Propellant Ignition and Combustion Research; New Tools and New Directions

12. PERSONAL AUTHOR(S) Alexander, M.H.; Dagdigian, P.J.; Jacox, M.E.; Kolb, C.E.; Melius, C.F.; Rabitz, H.; Smook, M.D.; Tsang, W.

13a TYPE OF REPORT
Study Group

13b TIME COVERED
FROM ________ TO ________

14 DATE OF REPORT (*Year, Month, Day*)
89/2

15 PAGE COUNT
78

16 SUPPLEMENTARY NOTATION
Prepared by the US Army Research Office Study Group on Energetic Materials Combustion, 30 May - 3 June, 1988, Chapel Hill, NC Co-Chairmen, H. Rabitz, C. Kolb

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
Propellant, Combustion, Ignition, Model, Kinetics, Spectroscopy

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

The efficient and successful design of new generations of highly energetic propellants based on evolving nitramine chemistry will require a thorough knowledge of the chemical and physical parameters controlling their ignition and combustion.

The necessary level of insight can be attained and successfully embodied in the predictive computer models necessary for effective propellant design, development and testing activities if a coordinated, hierarchical program of theoretical modeling and confirming and supporting experiments is designed and properly executed.

This paper reviews the current state of our understanding of the chemistry and physics of nitramine propellant ignition and combustion and develops and motivates the basic research program necessary to put advanced nitramine propellant development on a firm and effective scientific basis.

(Continued on Reverse)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Robert W. Shaw

22b TELEPHONE (*Include Area Code*)
(919) 549-0641

22c OFFICE SYMBOL
SLCRO-CB

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

Block No. 19 Continued

Confronting and solving problems involving complex physicochemical phenomena which intertwine complex heat, mass and radiative transfer processes with chemical kinetics is a challenge which physical and engineering scientists are becoming much more adept at meeting. Modern theoretical and experimental tools are now available which allowed the design and utilization of much more adept at meeting. Modern theoretical and experimental tools are now available which allow the design and utilization of much more comprehensive analytical models as well as their concomitant supporting and confirming experimental measurements. Significant recent progress on these types of complex problems in the fields of atmospheric chemistry, hydrocarbon combustion chemistry, chemical laser development and advanced materials processing lead us to believe that similar, focused efforts on advanced nitramine propellant development will be both timely and fruitful.

US ARMY RESEARCH OFFICE TECHNICAL REPORT

NITRAMINE PROPELLANT IGNITION AND COMBUSTION RESEARCH: NEW TOOLS AND NEW DIRECTIONS

M.H. Alexander, Professor of Chemistry, University of Maryland
P.J. Dagdigian, Professor of Chemistry, Johns Hopkins University
M.E. Jacox, Research Chemist, National Institute of Standards and Technology
C.E. Kolb, President, Aerodyne Research, Incorporated
C.F. Melius, Combustion Research Facility, Sandia National Laboratory
H. Rabitz, Professor of Chemistry, Princeton University
M.D. Smooke, Professor of Mechanical Engineering, Yale University
W. Tsang, Research Chemist, National Institute of Standards and Technology

FEBRUARY 1989

89 2 10 004

ABSTRACT

The efficient and successful design of new generations of highly energetic propellants based on evolving nitramine chemistry will require a thorough knowledge of the chemical and physical parameters controlling their ignition and combustion.

The necessary level of insight can be attained and successfully embodied in the predictive computer models necessary for effective propellant design, development and testing activities if a coordinated, hierarchical program of theoretical modeling and confirming and supporting experiments is designed and properly executed.

This paper reviews the current state of our understanding of the chemistry and physics of nitramine propellant ignition and combustion and develops and motivates the basic research program necessary to put advanced nitramine propellant development on a firm and effective scientific basis.

Confronting and solving problems involving complex physicochemical phenomena which intertwine complex heat, mass and radiative transfer processes with chemical kinetics is a challenge which physical and engineering scientists are becoming much more adept at meeting. Modern theoretical and experimental tools are now available which allow the design and utilization of much more comprehensive analytical models as well as their concomitant supporting and confirming experimental measurements. Significant recent progress on these types of complex problems in the fields of atmospheric chemistry, hydrocarbon combustion chemistry, chemical laser development and advanced materials processing lead us to believe that similar, focused efforts on advanced nitramine propellant development will be both timely and fruitful.

Gun propellants, Rocket propellants,
LOVA Propellants, Solid propellants,
RDX, HMX. (AW)

Table of Contents

4. Research Directions for Critical Combustion and Supporting Laboratory Experiments

5. Sensitivity Analysis as a Critical Cross-Connection

6. Conclusions and Recommendations

7. Acknowledgements

8. References

Figures

Tables

1. INTRODUCTION

1.1 Problem Background

Nitramine propellants are based on energetic chemical materials containing nitro groups chemically bound to other nitrogen atoms: $N\text{-}NO_2$. They are widely used in low vulnerability ammunition (LOVA) due to their low sensitivity to accidental ignition and in tactical rockets where they help to produce reduced smoke exhaust plume signatures.

Currently, the most widely used nitramine propellants are the cyclic compounds HMX (Octahydro - 1,3,5,7 - tetranitro - 1,3,5,7 - tetrazine) and RDX (Hexahydro - 1,3,5 - trinitro - 1,3,5, -triazine). However, new energetic nitramine compounds are being developed for use in energetic propellant binders. A particularly promising research area is the synthesis of new classes of caged nitramines in which the ring strain energy contributes significantly to the energy content of the molecule.

The safe and effective use of energetic chemical materials in gun and rocket propellants requires that their ignition and combustion characteristics be optimized to maximize reliable ignition rates and combustion heat release at a predetermined burning rate, while minimizing sensitivity to accidental ignition, degradation on storage, burning instabilities, erosive or corrosive exhaust products, and other undesirable properties. In particular, control of flame spread during ignition has been a major concern in gun propellants where stable and reproducible pressure rises are critical to achieve standardized projectile velocities and trajectories.

Gun and rocket propellants are formulated by combining energetic materials such as crystalline nitramines with polymeric binders that provide the necessary mechanical properties to form and sustain grain shapes and densities. Binder materials have a major impact on propellant ignition and combustion properties, as do stabilizers, plasticizers, and other propellant grain additives. Thus, in order to optimize overall propellant ignition and combustion performance, it is necessary to understand how to optimize pure nitramine properties as well as to understand the ignition and combustion properties of these other propellant components in both their neat and formulated states.

1.1.2 Previous Review Efforts

Considerable research effort has been expended on understanding the ignition and combustion of RDX and HMX propellants. Good overviews have been presented by Boggs[1] and Fifer;[2] while a great deal of work on the thermal decomposition of RDX and HMX has been reviewed by Schroeder,[3] Cook,[4] Suryanarayana et al.[5] and Dubovitskii and Korsunskii.[6] Most of the work tabulated in these reviews has focused on macroscopic properties such as burning and thermal decomposition rates as functions of pressure and/or temperature. However, these global properties do not reveal the fundamental processes occurring at a molecular level.

Obtaining molecular level information on nitramine ignition and combustion is not trivial. The chemistry of these processes is complex and it typically proceeds in very harsh and challenging environments, often characterized by high pressures, high temperatures, short time scales, thin reaction zones and very labile chemical species.

Recently, however, greater efforts have been expended to develop both the experimental diagnostics and computational models needed to probe and understand nitramine ignition and combustion. Two recent workshops sponsored by the Army Research Office have focused attention on the development of these tools.[7,8] The most recent insight gained from these efforts will be reviewed in Section 2 of this report.

1.1.3 Critical Problems and Challenges

In order to optimize propellants based on RDX and HMX, and, more importantly, to design successful new propellants using advanced, energetic nitramine compounds it is necessary to greatly increase our understanding of nitramine ignition and combustion processes at the molecular level.

Both the synthesis of new, higher energy nitramine compounds and their successful formulation and testing as advanced propellants are difficult, time consuming, expensive and even dangerous tasks. Thus, the development of a predictive capability which would provide insight into those molecular propellant ignition and combustion performance characteristics is extremely desirable. Such an advance would be invaluable in guiding nitramine propellant research efforts and would significantly shorten the time and expense of developing successful new nitramine propellant formulations.

An illustration of the complex physical and chemical processes which govern the ignition and combustion of a nitramine propellent is presented in Figure 1. The coupling of critical energy and mass transport processes with several regions of complex chemical change demands a sophisticated approach to the overall problem.

In particular, it is almost certainly necessary to determine the detailed chemical reaction mechanisms for nitramine ignition and combustion. For instance, recent kinetic modeling of an RDX flame (explained more fully in Section 2) has demonstrated the importance of detailed gas

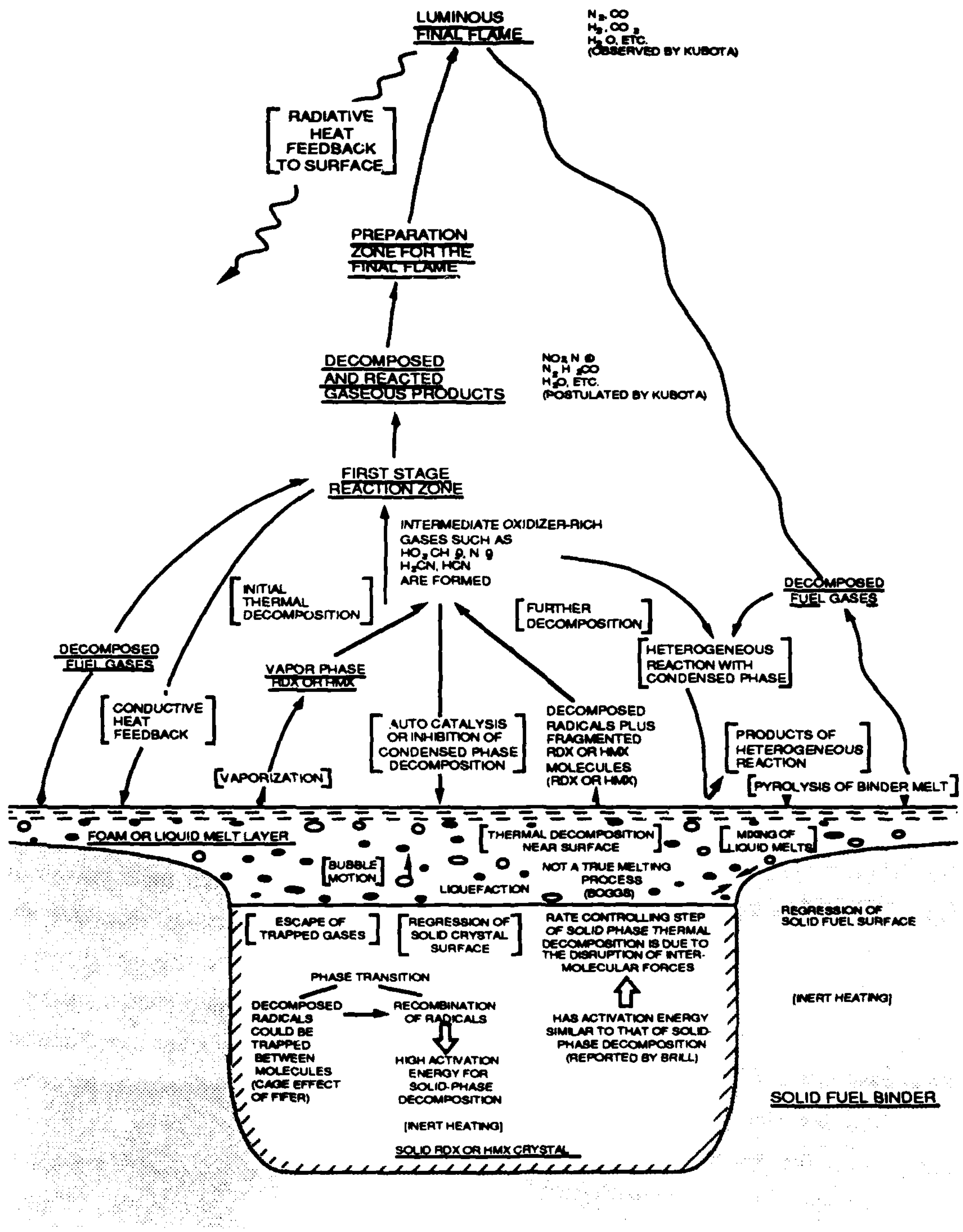

Figure 1. An Illustration of the Complex Physical and Chemical Processes which may Contribute to the Ignition and Burning of a Nitramine/Polymeric Binder Solid Propellant Formulation (Compiled by Prof. K.K. Kuo, Pennsylvania State University)

phase chemistry in controlling the burning rate. A key challenge is to identify the chemical species leaving the surface and to understand how they change as the molecular composition and physical formulation of the nitramine propellant and binder are varied. The presence of binders and additives may also increase the importance of condensed phase and surface reactions.

Critical research areas which must be addressed in any comprehensive nitramine propellant research program include:

1. The validity of existing gas phase reaction mechanisms
2. Extension of current reaction mechanisms to higher pressures
3. Extension of reaction mechanisms to include binder chemistry, particularly for new, energetic binders
4. Inclusion of new reaction mechanisms to treat new classes of nitramines (e.g., caged nitramines)
5. Elucidation and inclusion of elementary reaction steps to treat the initial condensed phase propellant melting and decomposition, vaporization, and flame formation processes
6. Reduction (lumping) of the validated set of reaction species and reactions to a small, yet mechanistically valid set for use in more global models
7. Extension of these reaction mechanisms for different time scales including the deflagration to detonation transition (DDT)
8. Extension of these reaction mechanisms to treat diffusion flames
9. Extension of current one dimensional models to include two and three dimensional effects

1.2 Study Group Overview

1.2.1 Identity and Purpose

Recent and anticipated advances in the theoretical and experimental tools which can be applied to a complex physicochemical problem such as nitramine ignition and combustion offer great promise. However, the power of these new techniques demands that a careful, general plan of research be formulated and pursued. This is due to the highly interactive and interdependent nature of modern multi-disciplinary research efforts.

In order to review the current state-of-the-art in nitramine propellant ignition and combustion research, to define the field's critical research challenges, and to design an overall research plan which utilizes the power of current and anticipated advanced research tools, the

Army Research Office assembled a small study group of experimental and theoretical research scientists in late May and early June of 1988.

Study group members included M.H. Alexander, University of Maryland; P.J. Dagdigian, Johns Hopkins University; M.E. Jacox, National Bureau of Standards (now the National Institute of Standards and Technology (NIST)); C.F. Melius, Sandia Livermore National Laboratory; M.D. Smooke, Yale University; and W. Tsang, National Bureau of Standards (NIST). The study group was chaired by H. Rabitz of Princeton University and C.E. Kolb of Aerodyne Research, Inc. Expert briefings were provided by K.K. Kuo of Pennsylvania State University, R.A. Yetter of Princeton University, and R.A. Fifer and G.F. Adams of the U.S. Army Ballistic Research Laboratory.

This paper presents the study group's assessment of our current understanding of the basic physics and chemistry of nitramine propellant ignition and combustion and outlines a basic research program which we believe will generate the knowledge and understanding necessary to allow systematic development of new energetic nitramine propellants.

1.2.2 Relation of Nitramine Propellant Combustion to Other Problems

It is important to recognize that nitramine propellant ignition and combustion are examples of many complex physicochemical processes which have demanded the research community's attention in recent years. Problems of similar complexity, where multicomponent chemical kinetics are coupled to energy and mass transport, are now becoming regular fare. Concerted programs combining theoretical modeling and analysis, directed molecular level laboratory experiments, basic theory, and difficult macroscale measurements have been mounted with considerable success to address problems as diverse as stratospheric ozone depletion,[9,10] the scale-up of hydrogen and deuterium fluoride chemical lasers,[11,12] the optimization of silicon chemical and plasma vapor deposition reactors,[13,14] and the analysis of hydrocarbon combustion systems and their concurrent pollution formation mechanisms.[15,16]

Experience gained and lessons learned in the performance of these programs should have a clear impact on the research plan for a nitramine propellant ignition and combustion research program.

1.2.3 Hierarchical Research Structure

Almost all practical problems in combustion are recognized to involve complex interactions of chemistry with heat, mass, and radiation transport processes. Furthermore, the chemistry controlling the combustion processes is often a melange of molecular structure and molecular energetics issues, which control the thermochemical aspects of combustion; and molecular dynamics and chemical kinetic processes, which, in turn, strongly affect the rates of ignition and combustion processes, and thus the rate of energy release.

The complex nature of combustion phenomena usually requires combustion scientists and engineers to build and validate quantitative, macroscale models to allow the effective design and scaling of combustion devices and related equipment. These macroscale models, in turn, require the input of numerous molecular or microscale parameters such as: reaction rate constants and mechanisms; enthalpies and entropies of vaporization, reaction and condensation; radiative emission and absorption cross sections; and turbulent mixing parameters. Each of these microscale input variables must be obtained from dedicated experiments and/or theoretical models or estimates.

Any comprehensive combustion research program should be driven by an interplay of macroscale model predictions and macroscale experiments which have been designed and analyzed by exercising the macroscale models. However, it is generally critical that key uncertainties in lower scale mechanisms and input data be constantly evaluated and improved, otherwise models may never faithfully represent reality. Figure 2 illustrates the hierarchical, but strongly interconnected and interdependent, multilevel structure of research and development activities necessary to tackle a complex combustion process like nitramine propellant ignition and burning.

The research activities below the dashed line in Figure 2 are the focus of the balance of this report. However, the interface between research and new propellant design, development, and testing activities represented by the dashed line is also critical. Without a strong tie to the traditional propellant development community no research program can achieve a significant impact.

1.2.4 Role of Sensitivity Analysis

During the past decade significant progress has been made in applying systematic sensitivity analysis techniques to macroscale combustion models in order to quantify the extent to which model output predictions depend on both macrosystem boundary conditions and microscale input parameters. Such sensitivity analyses can be used to identify the microscale mechanisms and input parameters most in need of better experimental and/or theoretical quantification. Furthermore, it is now recognized that much of the theoretical modeling activity used to predict microscale molecular structure and dynamics can also be assessed and improved using demonstrated sensitivity analysis techniques. Finally, sensitivity analysis can be used to design better experiments at both the macroscopic and molecular scales, and to aid in reducing model parameter sets to produce tractable higher level models.

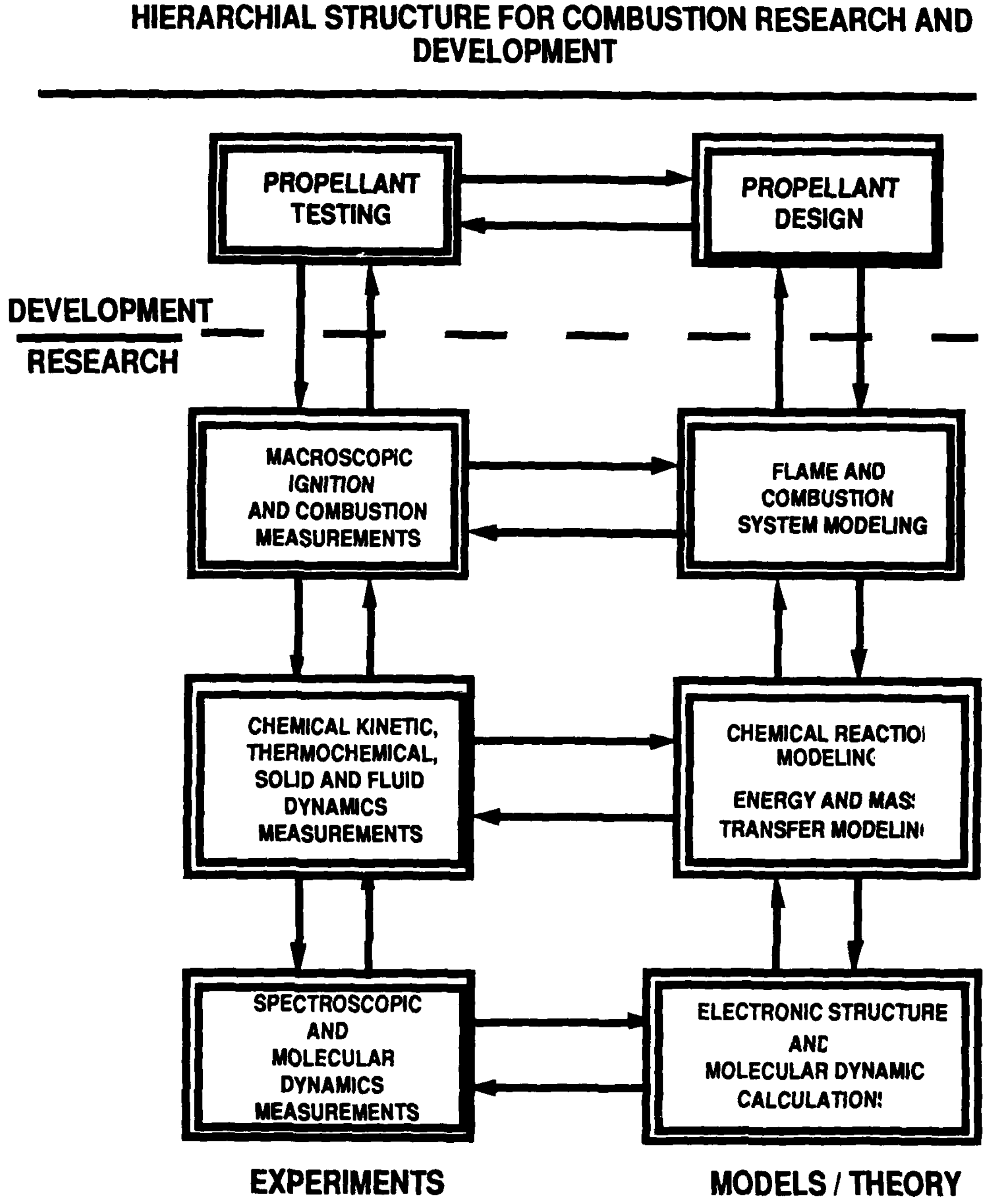

Figure 2. A Schematic of the Desired Herarchical Structure of a Coordinated Research and Development Program for Solid Propellant Combustion Research.

Used in all these guises, it is clear that systematic application of sensitivity analysis can provide a critical component of the interconnections illustrated by the arrows in Figure 2.

1.2.5 New Tools and New Directions

The message this paper hopes to convey is straightforward: complex physicochemical problems such as nitramine ignition and combustion are now amenable to systematic exploration and elucidation. A closely coordinated plan involving hierarchical experimental and theoretical activities can and should be developed to guide research on present and future nitramine based propellants.

Driven by impressive and on-going advances in both computational machinery and algorithms and experimental diagnostics, the advanced research tools needed to grapple with complex problems such as nitramine combustion are available or can be developed. More detailed discussions of the tools we now have, or are forging, can be found in Section 3 (Theory/Modeling) and Section 4 (Experiments/Diagnostics).

The studies made possible by this modern tool kit, properly coordinated and motivated by comprehensive models and concomitant sensitivity analyses, are capable of providing the insight and the technology base necessary for the design, testing, and implementation of optimized, energetic propellants based on nitramine chemistry.

2.0 FUNDAMENTAL CHEMISTRY AND PHYSICS OF NITRAMINE IGNITION AND COMBUSTION

2.1 Existing Nitramine Combustion Models

Detailed chemical kinetics mechanisms of ignition and combustion are not well known for any of the energetic propellants, although global chemical mechanisms exist for some types of propellants. For example, it has been established that the global chemical pathway for the combustion of double-base propellants involves: nitrate ester $\rightarrow NO_2 \rightarrow NO \rightarrow N_2$.[2]

For common nitramine propellants, even this global understanding was lacking until recent detailed chemical kinetics modeling efforts.[17-19] Previously, it was presumed that the combustion process evolved through the formation of N_2O and that CH_2O played an important role. A more definitive picture now exists due to models of RDX flames by Melius.[17,18] Utilizing a thirty-one species model containing 137 reactions, he has been able to reproduce a variety of experimental observations, including species profiles for a 0.05 MPa RDX flame as well as its flame speed and pressure dependence.[18]

The success of this model is partially due to earlier extensive studies on NO_x destruction and formation in hydrocarbon flames by the combustion community. As a result, an extensive data base of kinetic rate expressions now exists for the thermal processes which are directly pertinent to the RDX decomposition flame. The utility of these data in understanding nitramine combustion is a striking demonstration of the power of the generic approach to the solution of such problems. That is, properly determined and evaluated elementary rate expressions can be ported into descriptive kinetic models to successfully describe a wide variety of combustion and related reactive processes.

The partial success of Melius' ambitious initial (and necessarily still incomplete) models illustrate the utility of fundamental approaches to studying nitramine decomposition. In the past there have been many engineering models of the RDX decomposition flame which contain extremely simplified chemical mechanisms which were derived essentially as parameter fits. For some applications such "data fits" are all that is needed, however, the range of applicability of such models is always uncertain. With a correct fundamental kinetic model one should be able to replicate the full range of phenomena where chemistry is an important factor. These include the effect of binders, thermal stability and ignitability. After having achieved a comprehensive detailed chemical kinetic model, one can then reduce the number of equations by lumping the dependent variables to create useful engineering models.

2.2 Current Understanding of Ignition and Flame Chemistry

In recent years there have been several very complete reviews on nitramine decomposition.[3] Many of the most sophisticated modern techniques have been used to determine the nature of the reaction products and complete lists of reaction products have been compiled.[2] It is clear from even the most cursory analysis that nitramine decomposition involves unique features that are not observed in more familiar hydrocarbon decomposition systems. The unraveling of this "new chemistry" represents a major intellectual challenge in the study of such systems. From a practical viewpoint any "correct" model must be able to account for these observations.

Unfortunately, many earlier studies were flawed by a lack of the sensitive diagnostics available to more current workers; thus, many of the species that must have been present were not detected. Furthermore, the importance of isolating initial steps for careful study was not realized; nevertheless, important mechanistic features were uncovered.

For example, the isotopic labeling work of Suryanarayana et al.[5] on RDX and HMX have established that the decomposition products N_2 and N_2O consist of one N from the ring and the other from the nitro group. The nitrogen in HCN is exclusively from the ring, while that in NO is from the nitro group. These set important constraints on the nature of the reaction pathways, suggesting that the possible depolymerization product, $H_2C{=}NNO_2$, undergoes molecular decomposition to form formaldehyde and N_2O. Unfortunately, theoretical thermochemical investigations by Melius and Binkley have not been able to identify a likely reaction pathway.[20] As a result, Melius was forced to propose a more complex reaction pathway involving the original ring structure.[17,18]

In the past two years, increasingly powerful combustion probes and greater sophistication in their application have led to a number of extremely interesting observations bearing on the initial steps in RDX decomposition. Obviously, knowledge of these decomposition pathways is of prime importance in any detailed chemical model. Lee and co-workers have demonstrated from the analysis of products arising from the infrared multiphoton decomposition of RDX in molecular beam experiments that concerted reaction to form $H_2C = NNO_2$ is the predominant decomposition pathway.[21]

Lloyd et al. have determined a rate expression for the breaking of the N-NO_2 bond from the static pyrolysis of dimethylnitramine.[22] Their data together with the earlier data of Flournoy[23] now satisfactorily span the temperature range of 460-960 K. Even more impressive is the very good concordance between their rate expression and that derived by Robertson on the decomposition of RDX in trinitrotoluene (TNT) solution carried out over 40 years ago.[24] This suggests that even in the very polar medium of TNT the RDX decomposition mechanism remains unchanged; this has important implications about RDX decomposition mechanisms in the condensed phase. Unfortunately, a major discrepancy remains between their bond breaking mechanism and the mechanism favored to explain Lee's molecular beam observations. Moreover, Laser Powered Homogeneous Pyrolysis[24a] studies provide evidence for a nitro-nitrite rearrangement in competition with bond breaking. This is in seeming disagreement with the results of Lloyd[22] and has not been observed in molecular beam experiments. The resolution of such problems must be an important task of any research program on nitramine decomposition.

We have noted the successful modeling effort of Melius on the RDX decomposition flame based largely on the set of thermal rate data gained from studies of NO_x formation and destruction in high temperature combustion systems. There is also a rich store of lower temperature kinetic data on the NO_x chemistry of pertinence to stratospheric and tropospheric pollution. Such data must, of course, be extrapolated to the high temperatures of interest for the present application. In a similar fashion, interest in hydrocarbon combustion has led to the development of an extensive chemical kinetic data base of the elementary reactions of the pertinent processes. Much of this data is directly applicable to the proper description of binder combustion.

Thus, there is a large volume of kinetic data that can be used to further our understanding of many aspects of nitramine decomposition. Nevertheless, there remains a need for data bearing directly on the nitramines and their immediate decomposition products. Advances in theoretical chemistry provide an important tool for filling some of these gaps. It is clear that for small and intermediate sized compounds satisfactory predictions can be made with respect to the thermodynamic properties of reaction intermediates. There are also indications that transition state structures and energies can be calculated with considerable accuracy. The recent theoretical paper by Melius and Binkley on nitramines and their decomposition products represent an important contribution in this area.[20] Combining this with the group additivity (to extend coverage to the large molecules of interest) and thermo-kinetic concepts of Benson[67] should provide a powerful methodology for setting limits to the possible range of rate constants and, in selected cases, making satisfactory predictions.

To sum up, there is at present a wealth of empirical observations from the older literature. These are difficult to interpret because of insufficient attention to systematic variations in reaction conditions necessary to unravel reaction mechanisms. New data from more direct studies, using modern diagnostics that permit more direct interpretation are beginning to appear. This has led to an important controversy on the nature of the initiating process for RDX. For many of the other processes, fundamental information developed for the modeling of high temperature NO_x reactions as well as stratospheric and tropospheric pollution and new developments in the proper use of theoretical chemistry can and have been successfully used to reproduce certain aspects of RDX combustion. We now have a basis for establishing plausible mechanisms and providing a listing of compounds whose reactions must be considered in the modeling of RDX combustion.

These techniques still, however, must be extended to nitramines more complicated than the relatively simple RDX molecule. The theoretical and experimental methods available to accomplish this task are discussed in Sections 3 and 4, respectively.

2.3 Current Modeling Approaches for Propellant Ignition and Combustion

Recent models of nitramine combustion have emphasized the importance of gas phase chemistry.[17-18] The work has paralleled the traditional approach used by combustion scientists in the study of hydrocarbon flames. In particular, two related models have been employed. In the first model the temporal behavior of the ignition of gaseous RDX was studied by solving time-dependent, coupled initial value problems for the temperature and the species mass fractions.[17] In the second case, one-dimensional premixed flame models were utilized to determine both the flame speed and the temperature and species mass fraction profiles as a function of the distance above the propellant surface.[18] As many as 50 chemical species with over 200 elementary reactions were included in these studies. This work clearly illustrated the importance of the choice of the transport and chemistry approximations in the prediction of the coupled effects of heat and mass transfer with chemical reactions in nitramine combustion.

The flame models employed by Melius balanced convective and diffusive transport with chemical production.[17,18] In particular, the diffusion velocity of the k^{th} species was modeled by assuming a Fickian relationship and a Curtiss-Hirschfelder approximation. The binary diffusion coefficients were computed from kinetic theory expressions. The thermal conductivity in the model was formulated by considering translational, vibrational and rotational effects. Of critical importance to these approximations was the choice of the Stockmayer potential parameters. For example, well depths, average collision radii, dipole moments, polarizabilities and rotational relaxation collision numbers for each species were needed. In some cases these quantities were estimated.

The models also required thermochemical data for the evaluation of heat capacities and enthalpies of the individual species. The reaction mechanism in the combustion of nitramine was modeled as proceeding through a multistep sequence of elementary reversible reactions. The intermediate species in such mechanisms are of extreme importance. They are involved in the chain initiation, chain propagation, chain inhibition and chain breaking reactions that describe the oxidation of a given fuel. From Melius' work it is clear that the choice of the pre-exponential factors, the temperature exponents and the activation energies are all of critical importance in gas phase propellant modeling.

The governing conservation equations were solved by a combination of time-integration and Newton's method. Because of the Arrhenius reaction rate terms, the equations were highly nonlinear; and a sufficiently "good" starting estimate from which Newton's method would converge was, in general, not available. Therefore, a transient solution was followed until it was in the convergence domain of Newton's method. However, because of the high gradients in both the primary and secondary flame zones, the initial computational mesh that was used in the calculation was not sufficiently refined in these regions. Hence, the mesh was adaptively determined. The combination of time integration, Newton's method and adaptive mesh refinement results in an extremely powerful technique by which to study nitramine decomposition.

The ignition and flame modeling techniques currently being used to study nitramine systems are standard methods capable of adequate representation of simple time dependent or one-dimensional flame behavior. In order to adequately represent the full range of chemical and physical processes represented in Figure 1, more sophisticated models of higher dimensionality will be required. The road to these models is discussed in Section 3.

3.0 RESEARCH DIRECTIONS FOR IMPROVED MODELS AND SUPPORTING THEORY

3.1 Extension of Chemistry Models

An essential ingredient in the quantitative description of any complex chemical phenomena is an evaluated chemical kinetic data base. This is the set of "best available" rate expressions for the reactions of all the species that are of importance in describing the chemistry of the process. Although such a data base does not now exist for any aspect of nitramine decomposition, they have been developed for stratospheric and combustion chemistry.[25] The basic approach is therefore well established and is described below.

It is important to realize that for any complex chemical process, the number of elementary reactions always exceeds the number of observables that can be measured to validate the model. It is therefore often possible to fit a particular set of data if one treats the chemical kinetic parameters arbitrarily. This may be satisfactory as a testing procedure for real devices or prototypes, but it clearly has no predictive value and is completely unsatisfactory for the scaling of laboratory results to the field situation. Thus, correct rate constants must be used and all possible reactions considered. Leaving out a reaction is equivalent to the assignment of a zero rate constant, just as omission of a species assumes that its concentration is zero at all times. On the other hand, one cannot simply include species and reactions in an arbitrary manner since the already large data base will become so enormous that it will prevent proper evaluation and validation.

Figure 3 contains a recommended listing of the reactants that should be considered in any chemical kinetic data base for RDX decomposition. RDX is used here as an example, but similar listings can be drawn up for other nitramines. The generic nature of this approach means that there will be a great deal of overlap.

The layout of the species list is based on a conceptual mechanism which is consistent with an analysis of the existing knowledge, as discussed in Section 2. Summarizing briefly, it involves initial decomposition of RDX either by N-NO_2 bond fission or by concerted depolymerization. For the former this will result in the formation of a nitrogen centered free radical. At sufficiently high temperatures successive beta bond fission will lead to the formation of two H_2CNNO_2 molecules and one H_2CN radical.

Note that under certain circumstances the current controversy on the initial reaction pathways is immaterial, since each will lead largely to the same reaction products. However, if beta bond cleavage is sufficiently slow, then the nitrogen centered RDX radical can abstract a hydrogen atom, add to NO to form the nitroso compound, or react with NO_2 to form the nitrite, which will rapidly decompose to form the nitroxide.

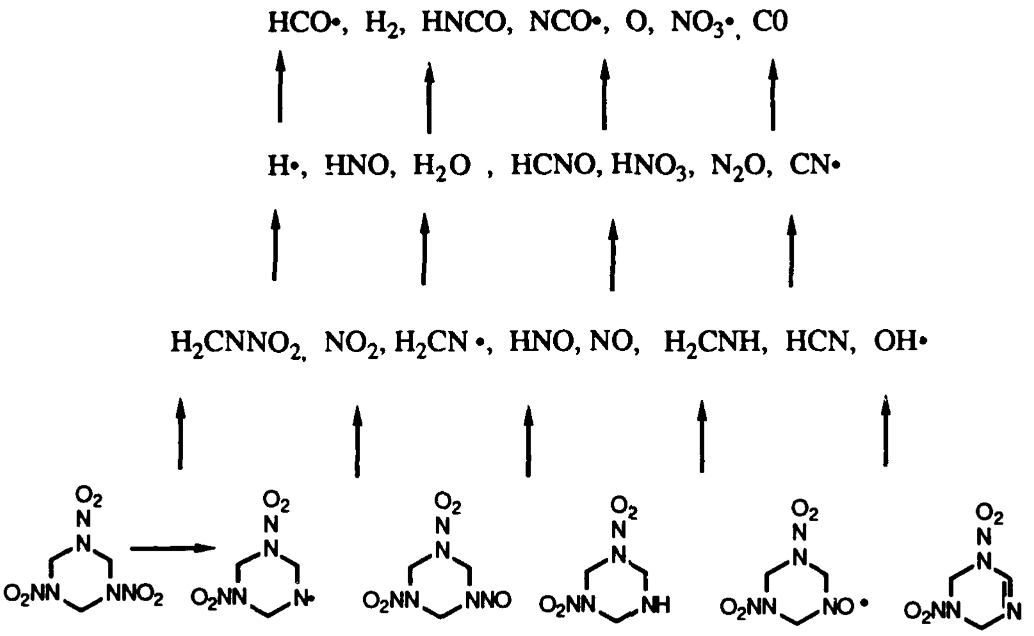

Figure 3. Conceptual Mechanisms for RDX Decomposition and Combustion

Of course, once reactive free radicals are present in the system, hydrogen atoms can be abstracted from the carbon in RDX. Since the N-NO_2 bond beta to the radical site has virtually no bond energy it can immediately form the ringed imine structure. One can proceed in this fashion and obtain 16 ringed structures with increasingly higher degrees of unsaturation. However, we do not feel the need at this stage to consider all the possibilities, since ring breaking will be occurring in parallel with these processes and there will be, with time, smaller numbers of ring structures to destroy. A similar rationale leads to the inclusion of the smaller species.

In general, the higher the compound is in the listing in Figure 3, the later its stage of formation in the combustion process. It is encouraging that our analysis of the data leads to virtually the same type of species as selected independently by Melius.[17,18] This is an indication that the existing data limit us to a fixed set of possible mechanisms. We emphasize that nothing precludes us from expanding this set of molecules or, for that matter, eliminating compounds to be considered. For instance, the addition of hydrocarbons will bring binder chemistry into the picture. (Note that many of the elementary reactions pertinent to binder combustion have already been evaluated in the course of the development of the hydrocarbon data base.[25]) In a similar fashion we can cover formulations for other propellants by the addition of appropriate species. This will always require the addition of a smaller reaction set, since many of the reactions are already included.

Having decided on the species to be included, it is necessary to evaluate all possible elementary thermal reactions among the species, as well as all unimolecular processes. For this purpose a reaction grid is a very useful bookkeeping device. An example, for RDX, is shown in Figure 4. Such a procedure guarantees that no possible reaction will be neglected. Formally there are 390 interactions to be considered. There are, however, many processes that need not be considered in detail, since their potential products are either thermochemically or mechanistically improbable. Thus, a cursory inspection suggests that the actual data base for this application will involve about 200 interactions. It will be noted that Figure 4 first contains a listing of molecules involving the reactions of formaldehyde and its decomposition products. This data sub-set has already been evaluated in the context of work on hydrocarbon combustion.[25] This illustrates once again the advantages of a generic approach. The second and fourth groups consist of reactions that are of importance in NO_x formation and destruction, many of which have been addressed experimentally. These reactions form a major basis of Melius' modeling efforts;[17,18] nevertheless, relatively few of these measurements have been properly evaluated. The third group of interactions represents the true challenge in nitramine chemistry, since very few of the processes that are listed have been measured and their rate parameters must be estimated for current modeling efforts. These reactions are of key importance in the initial states of nitramine decomposition and therefore impinge on the whole range of phenomena associated with ignition and sensitivity. They should prove to be a severe test of our ability to make kinetic rate parameter estimates.

3.2 Improvement of Kinetic Rate Parameters

3.2.1 Measured and Evaluated Rate Data

Past work on the development of the stratospheric and combustion data bases have established basic procedures for evaluating, extrapolating and estimating chemical kinetic data. They involve a critical examination of all the pertinent experimental work. First preference is

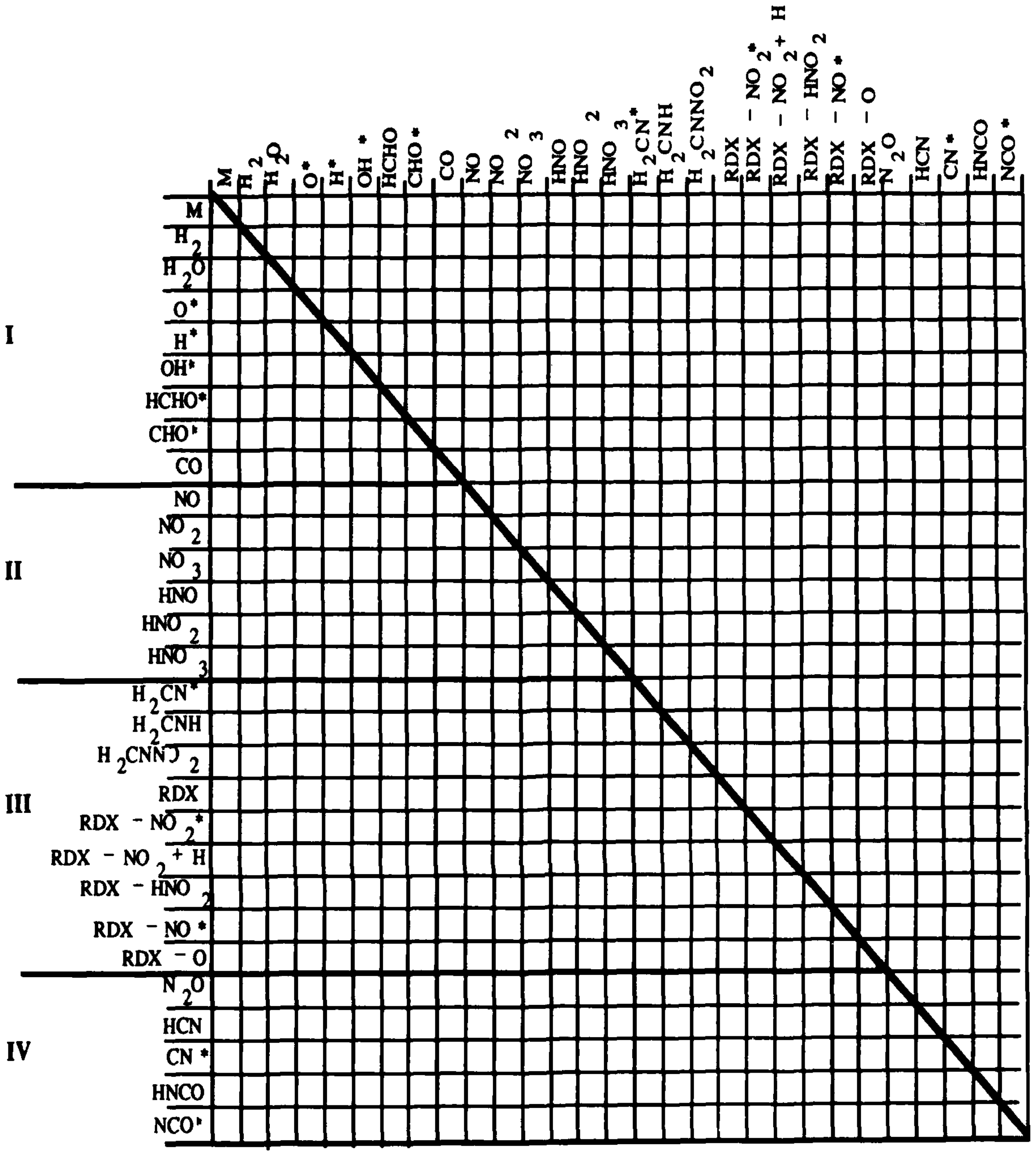

Figure 4. Possible Reaction Grid for RDX Decomposition. Interactions to be considered are below the Diagonal Line. Group I Interactions are in the Hydrocarbon Combustion Data Base. Reactions in Groups II and IV Contain NO_x Formation and Destruction Processes. Group III Reactions are Generic to RDX.

given to measurements where there are no mechanistic uncertainties. Frequently, this is from direct determinations of the rate of disappearance and appearance of reactants and intermediates in real time.

There is, however, no substitute for good experimental design. Indeed, it has been found that in more complex situations where careful and complete final product analyses are carried out very reliable results can be obtained. In many cases these may not be individual rate constants, but accurate ratios of rate constants. From data of this type it is still possible to generate an accurate network of rate constants in the absence of direct measurements.

As the data base expands it is possible to derive from these networks increasingly more accurate new values. In the absence of kinetic data, thermodynamic considerations in the form of detailed balance are used. In other cases, rate constants are assigned on the basis of analogy or thermokinetic information. In all cases it is necessary to assign an uncertainty limit; furthermore, it should be realized that this is a subjective number. To a considerable extent it is based on the evaluator's judgement and past experience, as data sets are intercompared with considerations imposed by reaction mechanisms and constraints imposed by thermodynamics and reaction rate theory kept in mind. Practically, this means that the user should feel free to adjust the rate constant in his model within the evaluated limits.

In the past, rate theory was used in data evaluations purely as a method of extrapolation. For metathesis reactions involving H atoms the bond-energy bond order (BEBO) method of Johnston[26] was used to derive transition state structure or, alternatively, the curvature of the Arrhenius plots for these reactions. In general, these lead to a temperature dependent A-factor in the T^2 to T^4 range, where the smaller values are characteristic of atoms and larger values of polyatomics; this is fully consonant with thermokinetic considerations. For nitramines, the theoretical approach of Melius and Binkley presents the evaluator with a powerful new tool.[20] This should be employed in any data evaluation or prediction activity.

Unimolecular reactions in the broadest sense, including not only decompositions or isomerizations but also combination and chemical activation processes, are rendered more complex than metathesis reactions by their dependence not only on temperature but also on the nature and pressure of the bath gas. There is a fully developed calculational method, the RRKM procedure, which provides a framework for projecting data over all relevant pressure and temperature ranges.[27] The inputs to this type of calculation are the high pressure rate expression for unimolecular decomposition and the average step size down. The general technique has been applied to a large number of such reactions in the course of the development of the hydrocarbon combustion data base and has proved to be extremely satisfactory in tying together data obtained under a wide variety of conditions.

For bond breaking reactions, the high pressure activation energy is the bond energy and is thus related to the heat of formation of the organic radical fragments. In the present application the thermodynamic properties calculated by Melius and Binkley[20] can substitute for the more direct determinations that have been used in the past. Similarly, for complex fragmentation, the theoretical calculations offer a means of estimating high pressure rate expressions in the absence of direct data.

Implicit in all the above is the assumption that thermal rate constants are the appropriate values to use in the modeling of nitramine decomposition processes. This assumes that the reacting molecules are in a Boltzmann distribution. For the pressures at which nitramine decompositions are usually carried out this must be the case, except for unimolecular decomposition processes at very high temperatures. Here the depletion of the upper levels by decomposition is taken care of by the RRKM calculational procedure.

More serious is our assumption that a standard gas kinetic treatment is adequate. There are two scenarios that must be considered: a) the possibility of condensed phase reactions mediating solid propellant decomposition and vaporization, and b) condensed phase behavior at the high fluid pressures that are generated in gun barrels. For example, more recent efforts by Melius have drawn attention to the occurrence of substantial decomposition in the condensed phase (particularly for HMX) and to the intermediacy of N_2O in the decomposition. Under these conditions he has suggested that an H_2O catalyzed N_2O elimination from methylene nitramine could, in the condensed phase, alleviate the problem of forming N_2O through a highly strained four membered ring. This reaction could be viewed as a sequence of two concerted reactions, or as an acid catalyzed process. All of these possibilities can be subject to experimental tests. On the other hand, for applications such as flame speed modeling condensed phase reactions simply alter the boundary conditions for vapor phase modeling.

The role of theoretical chemistry in the evaluation of chemical kinetic data will be discussed further in the following subsection. The importance of a reliable theoretical foundation for rate data evaluation is underlined by the many references to the work of Melius and Binkley.[20] While this approach is satisfactory for most thermodynamic properties, there is less certainty for transition states. Validation and extension of the procedure in such cases would be extremely valuable. In the area of molecular dynamics, the proper treatment of tunneling is key to the extrapolation of low temperature data to nitramine decomposition situations. The present methodology for treatment of such systems is basically by analogy and is therefore unsatisfactory.

It is important to realize that the evaluation data base produced in this manner provides at best a snapshot of the present state of experimental and theoretical understanding of the issues in question. There is no substitute for adequate state-of-the-art experimental and theoretical work. Evaluated rate data do, however, serve as a focus for further basic research efforts.

It is essential that all simulations must be based on the same data base. Through the utilization of appropriate sensitivity analysis techniques this will lead to the determination of the key controlling reactions of pertinence to any particular application. This combination of evaluated rate data and model sensitivity analysis will encourage experimentalists to take a closer look at the rate constants for such processes and any errors in our evaluation will be immediately revealed. Thus, through iteration an optimum chemical data base will be established.

We conclude with a number of critical issues that impinge on our proposed mechanisms. First, a large portion of our mechanistic deductions are based on the results of Suryanarayana et al.[5] The nature of any postulated mechanism will be drastically changed if these results are incorrect or not applicable. A confirmatory study is therefore badly needed. We have previously outlined the present controversy on the initial processes during RDX decomposition (Section 2.2). This has very important consequences in the development of the reaction mechanism. Thus if depolymerization is the main initial step, the number of ring compounds that we should consider in our mechanism may be reduced. Furthermore, Melius' mechanism is unable to account theoretically for the reaction $H_2C{=}NNO_2 \rightarrow H_2CO + N_2O$; thus, the reduction of many of the ring intermediates will make it very difficult for him to account for the results of ^{14}N and ^{15}N labeling experiments. Note also, that the calculations of Melius and Binkley (Section 3.2.2) seem to rule out the depolymerization mechanism on thermodynamic grounds. Thus, if the published interpretation of the molecular beam experiments is correct, these calculations may have significant errors. H_2CN and HNO are clearly important reaction intermediates and we have virtually no experimental rate data on their stability and reactivity. Obviously, some careful experiments will lead to much greater confidence in any estimates. In a similar fashion, the presence of H_2CN will lead inevitably to H_2CNH formation. An important issue will then be the mechanism and rate constants for H_2CNH destruction.

3.2.2 Emerging Role of Theoretical Chemistry

Present day theoretical techniques can provide a powerful complement to experiment in unravelling the fundamental chemistry which occurs during decomposition and deflagration of nitramine based propellants. Theory is a full partner with experiment in unravelling the fundamental chemical mechanisms of flames. For example, theory can play an important role in the interpretation of spectroscopic flame diagnostics,[28,29] in expanding the necessary thermochemistry data base to species which may be experimentally intractable,[20] and in providing the framework for the extension of kinetic data to the high temperature, high pressure conditions which characterize exploding propellants. We discuss each of these areas in more detail below.

Currently operational ab initio techniques[30,31] can now accurately describe the ground and low-lying excited potential energy surfaces of the small polyatomic systems containing first row atoms which play a key role in both the primary and secondary flame zones in nitramine systems. For closed shell systems, which can be well represented by a single reference electronic configuration, self-consistent-field (SCF) - configuration interaction (CI) techniques can yield accurate energies and spectroscopic constants. For radicals and other open-shell species, it is often necessary to use a multiconfiguration SCF (MCSCF),[32-35] a complete active space SCF (CASSCF),[36] or a multireference configuration-interaction (MCSCF-CI)[30,31] description. A multireference capability also allows one to accurately treat excited as well as ground states of a particular symmetry, even when the underlying state of the isolated molecule cannot be well described by a single reference electronic configuration.

With analytic derivative capability, a single calculation can provide not only a point on a potential energy surface but also the gradient and second derivatives of the energy. This is extremely useful in obtaining spectroscopic parameters and locating transition states for reactions. Although large basis set CASSCF and especially MCSCF-CI calculations are expensive, particularly when a large number of reference configurations is required to accurately describe the electronic states in question, they can now be used selectively to obtain information on species which play a particularly important role. This was not possible even a few years ago.

One example is in the area of flame diagnostics. Suppose a transient radical has been identified as a possibly crucial intermediate. An example might be the methylene amidogen radical, H_2CN, which is believed to play an important role in nitramine decomposition. Before searching for this, or another, transient radical it is necessary to locate an electronic state which will either fluoresce [for laser induced fluorescence, (LIF)] or can be subsequently ionized [for resonance enhanced multiphoton ionization, (REMPI)]. In addition, one must determine the oscillator strength of the transition in question to convert spectral intensities to populations. Ab initio calculations can help in both of these problems. To calculate dipole oscillator strengths it is necessary to employ the same orbital basis for both the ground and excited electronic states. Suitable orbitals for this purpose can be obtained from state-averaged[35,37,38] MCSCF, CASSCF, or MCSCF-CI calculations.

Another use of ab initio calculations is in the determination of the heats of formation of the many unstable radicals, both large and small, which play a role in nitramine flames. If a rate constant for a particular reaction can be experimentally determined in one direction, but not in the other, the desired reverse rate constant can be determined if the heats of formation of both reactants and products are known. Over the past several years Melius has developed[31] a systematic procedure to calculate accurate heats of formation from SCF-CI calculations.[20] With the availability of more accurate MCSCF-CI techniques it will now be possible to improve this data base, for cases in which the bond additivity correction of Melius can not be applied with confidence.

Reactions are governed not only by thermochemistry, but also by the topology of the potential energy surfaces which lead from reactants to products. Transition state theory provides a means to predict the magnitude and temperature dependence of reaction rates from a knowledge of the energetics and the geometries of the one (or more) transition states which separate reactants from products. At a more sophisticated level, classical trajectory calculations or more complete semi-classical methods, supplemented by sensitivity analysis, can reveal how regions of the potential energy surface other than the transition state can influence rates of reaction.

The accurate location of transition states for a particular reaction may allow us to estimate product branching ratios when these are inaccessible experimentally and, furthermore, can provide a necessary check on experimentally determined activation energies. Since bonds are being broken and formed at a transition state, to describe these well it is crucial to use an ab initio technique which allows for the orbital distortion and changes in electron occupancies which accompany bond formation and breaking. This can be done only using multireference techniques. Analytic derivative techniques facilitate the location of transition states.

For example, the BAC-MP4 method developed by Melius cannot treat the reaction coordinate for the bond breaking of an energetic material to form NO_2, its possible recombination, or its rearrangement to form the nitrite. Yet these processes can be critical in the early stages of nitramine ignition and combustion. Further theoretical work on these classes of reactions must be pursued. Already, quantum chemists in the propellant community are addressing these reactions using the newer MCSCF computer codes developed at the U.S. Army Ballistics Research Laboratory and elsewhere. Examples of the use of MCSCF-CI calculations in the determination of transition states for polyatomic molecules crucial in nitramine decomposition is provided by the very recent work of Saxon and Yoshimine[39] on the nitro-nitrite rearrangement in NH_2NO_2 and by the work of Mowrey and Page[40] on the decomposition of CH_2NNO_2.

In the case of radical-radical reactions, the open-shell character of both reactants implies that the reaction can proceed over more than one potential surface. It is then even more important to be able to characterize all these surfaces, or, at a simpler level, all the relevant transition states. An illustration is given in Figure 5, which shows, schematically, some of the potential surfaces of relevance in the reaction: OH + N → H + NO, which is thought to be one of the most important reactions in NO formation in methane/air as well as other hydrocarbon doped flames. Exploratory model studies of Melius using sensitivity analysis have identified this reaction as being extremely important in the secondary flame zone in RDX combustion.[18] Spin coupling implies that the forward reactant can take place only on potential surfaces of triplet or quintet multiplicity.[41,42] There are two triplet surfaces which connect reactants and products, only one of which corresponds to the lowest ($^3A''$) states of the HNO and HON radicals. If total spin is conserved, then the quintet surfaces will be nonreactive; however, spin-orbit coupling can lead to reaction over the singlet surfaces which lead to the H + NO products, particularly if the singlet and triplet potential surfaces cross.

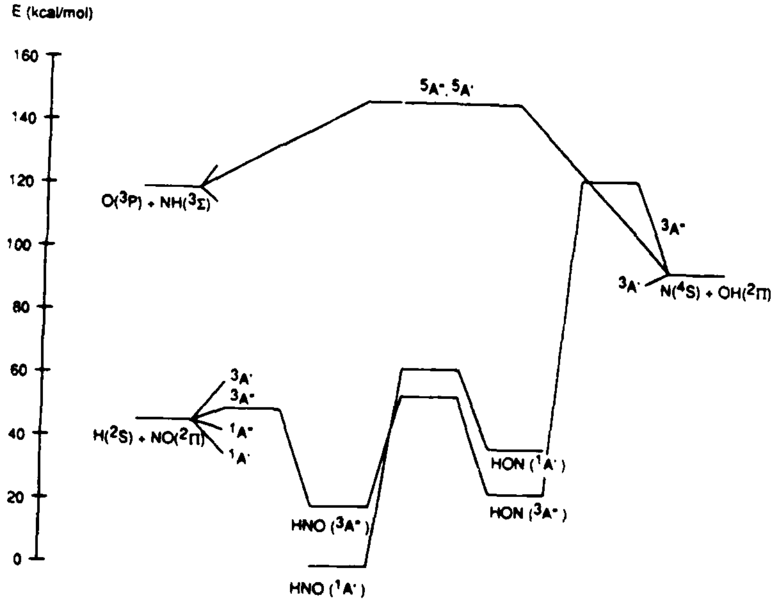

Figure 5. Schematic Diagram of the Lowest Potential Surfaces for the Reaction: N + OH ↔ H + NO. The Energies have been taken from the MP4-BAC calculations of Melius. The Heights of the Transition States are only Approximate. Note the Crossing Between the Lowest Singlet and Triplet Surfaces.

Since, as seen in Figure 5, the topology of radical-radical reactions is so complex, for even the simple N + OH reaction, the use of simple transition state theory to extrapolate experimental kinetic data for radical-radical reactions may lead to substantial error. What is needed are more sophisticated treatments of the collision dynamics for these systems which we hope will allow us to build models which can then be used in more global flame simulation studies.

One crucial question is how the initial reactive flux is partitioned between the various potential surfaces which separate from one another as the reactants approach. Simplistic models assume that this flux branching is purely statistical.[43] More accurate treatments must involve a careful consideration of the nonadiabatic coupling which occurs as the system passes from the asymptotic basis (in which the states correspond to products of the separated molecule wave functions) onto the various molecular surfaces. This will involve both the ab initio calculation of nonadiabatic coupling matrix elements (NACME's)[44-47] followed by the development of a simplified but accurate treatment of the dynamics at long range, where the flux branching will occur.

It is only recently that ab initio techniques have been developed to allow the calculation of the relevant NACME's.[44-47] Similarly, although there have been many studies of collisions between open-shell atomic species,[48-58] the corresponding full quantum formalism has not been successfully developed for collisions involving molecular radicals, particularly when reactive channels occur.

A similar, but equally important, problem involves the development of models to predict the rates of thermal decomposition processes which take place by spin-forbidden processes. An example might be the decomposition of HNCO:

$$\mathrm{HNCO}\ (^1A') \rightarrow \mathrm{NH}\ (X\ ^3\Sigma^-) + \mathrm{CO}\ (X\ ^1\Sigma^+) \quad ,$$

a reaction of considerable importance in the primary flame zone in nitramine flames. To treat this problem one must first be able to calculate spin-orbit coupling matrix elements for small polyatomic species.[59-61] Recent developments in quantum chemistry codes now provide this capability. Then one must be able to extend conventional RRKM theories[62,63] of unimolecular decomposition to the situation where the transition state arises from a crossing between two surfaces of different multiplicity. It will be important not only to carry out detailed calculations of decomposition rates for exemplary systems, such as the HNCO molecule, but also to develop parameterized models which can then be used both to predict decomposition rates for other, more complex molecules as well as to provide a mechanism for extrapolating laboratory experimental data.

Sensitivity analysis can also play an important role in theoretical reaction rate studies in several different ways. First, sensitivity analysis could be used to identify orbital structure or electron density regions of significance for dynamical or kinetic rates. This information could be used as feedback to improve electronic structure calculations. In a similar way, sensitivities could be calculated with respect to the location of points on a potential surface. Second, since transition state theory will likely be used to extract rate constants, a basic question arises as to why such an approach is only sensitive to the transition state region while in fact a full scattering or classical trajectory treatment will produce sensitivities over a broad region of the surface.

One final important role to be played by theory is in the development of models to understand how kinetic data obtained at atmospheric pressures can be extended to the extreme high pressure regimes which occur during propellant combustion. Particularly relevant will be the determination of how multiple collisions affect equilibrium constants, product branching ratios, and rate constants. Also necessary will be the investigation of how extreme pressures affect the excited state lifetimes, frequencies, and oscillator strengths of molecules which can be used in spectroscopic combustion diagnostics.

In summary, we believe that a more thorough computational effort should be undertaken using the state-of-the-art techniques mentioned above to describe both the relevant potential energy surfaces and the dynamics of the relevant reaction pathways for the following key and/or prototypical reactions:

$$H + NO, \quad H + NO_2, \quad HNO + HNO, \quad H_2CN + NO_2$$

As we have seen, theory has just now been developed to the point where major contributions can be made to expanding the existing molecular data base relevant to nitramine combustion. With appropriate support computational chemistry can continue to play an ever-expanding role. This will be enhanced as supercomputer technology continues to improve and becomes more widely accessible. As mentioned above, accurate calculations can now be carried out only on relatively small molecules. The advent of massively parallel computer architecture will allow us to address larger systems. Along with an increased effort in computational chemistry it is essential to continue to support work in basic theory, both in quantum chemistry and molecular dynamics. Only with this type of research can we develop the new models for nonequilibrium flame chemistry at extreme temperature and pressure.

3.2.3 Validation of Chemical Reaction Mechanisms

Detailed chemical kinetics models containing hundreds of reaction steps can provide tremendous predictive capability. However, they are always limited by the completeness of the reaction mechanisms and the accuracy of the rate constants. It is necessary to test the validity of the reaction mechanisms in the model, since some of the rate constants are likely to be incorrect or important reaction mechanisms may be omitted.

Key validation data can be obtained from flames, flow reactors, strand burners, shock tubes, and even static reactors. A more thorough discussion of appropriate experiments designed to yield model validation data will be presented in Section 4. Here it is only important to note that all serious models must reproduce relevant experimental measurements.

3.3 Improvement of Energy and Mass Transport Models

The accurate prediction of the transport properties (both diffusion and heat transfer) of the major and minor combustion species is crucial to our ability to model flames. All existing flame models make use of transport collision integrals[64] computed for spherical systems described by purely repulsive or Lennard-Jones 6-n or Stockmayer potentials. In nitramine flames, many of the major species (for example, H_2O, OH) are strongly polar and nonspherical. It is not yet fully known to what extent the diffusion or heat transfer cross sections will be affected by strong potential anisotropies or by the long-range dipole-dipole potential, which varies as R^{-3} instead of R^{-6} in the case of neutral atom interactions or R^{-4} in the case of ion-spherical atom interations.[65]

Since the rate of deflagration of a propellant is extremely sensitive to the rate of heat transfer to the surface from the high temperature flame zone, it is essential that the transport integrals used in flame modeling be as accurate as possible. With the computational resources presently available and with the accessibility of sophisticated codes to describe collisions between polar molecules,[66] theorists are now in a position to calculate collision integrals with realistic potentials.

3.4 Improvements in Thermochemical Data

In the previous sections of this paper we have highlighted the use of thermochemical data for a number of applications. It should be emphasized that thermodynamics represents the essential supporting structure for the simulation of any chemically reacting system. Aside from direct application, such as the determination of thrust, thermodynamics set the boundary conditions for any kinetic system. In certain situations a number of the reacting compounds may be in local thermal equilibrium leading to drastic simplifications of reaction pathways. Within the context of the kinetic processes, we note that detailed balancing (forward rate constant/backward rate constant = equilibrium constant) must be satisfied at all times. Indeed, as mentioned earlier it is frequently used to calculate the rate constant in one direction when that in the opposite direction is known.

Furthermore, much of our predictive capability in chemical kinetics is based on the use of thermodynamic properties and concepts as basic inputs. It is not accidental that the well known text on this subject by S.W. Benson is entitled "Thermochemical Kinetics."[67] For quantitative purposes particularly severe requirements are placed on the heats of formation of the species to be considered in any modeling effort. For example, at 500 K an uncertainty in the heat of formation of a radical species of 2.3 kcal/mol will lead to an uncertainty of a factor of 10 for the rate constant of a bond breaking process that leads to the formation of that radical.

For propellant decomposition, Figure 3, which applies specifically to RDX decomposition, is illustrative of the general classes of compounds to be considered. They can be divided into two broad categories. First there are the smaller species, many of which are of importance in NO_x formation, whose thermal properties are tabulated in the JANNAF Thermochemical Tables.[68] Much less satisfactory is the situation for propellants and many of their immediate decomposition products. In the case of RDX, the recommended value given in Pedley et al.[69] is 15.9 kcal/mol and is based on measurements carried out in 1942. A subsequent measurement[70] in 1956 derived a value of 12.9 kcal/mol. Certainly it should be possible to reduce this discrepancy. We suspect that for many other nitramines, particularly of the caged variety, the uncertainty may be larger.

In the prediction, assessment and extrapolation of kinetic data involving any given propellant discrepancies can be expected to propagate throughout the system. It will also have a direct effect on the thermodynamic properties of radicals derived directly from RDX. For example, the work of Lloyd and co-workers[2] have established the energy of a nitramine bond at 45 kcal/mol. On this basis the heat of formation of the hexahydro-3,5-s-triazyl radical is simply $- 45 + H_f(RDX) - H_f(NO_2)$ and error in the heat of formation of RDX will be directly reflected in that of the radical. Thus, there is a direct need for the accurate determination of the thermodynamic properties of propellant molecules. This should include both the enthalpy of formation and entropies. The longer range aim should be to develop a scheme for the prediction of the thermodynamic properties of the entire range of possible compounds. This will have to be based on an experimental and theoretical molecular mechanics program.

We next consider smaller molecular fragments. Typical species among the nitramines are H_2CN, H_2CNH, H_2CNNO_2 and some of the larger cyclic compounds in Figure 1. For the smaller compounds the work of Melius and Binkley[20] is of prime importance since it leads to direct prediction of thermodynamic properties. Nevertheless, experimental verifications, particularly a better estimate of the error limits, would be extremely useful.

Ironically, it is probably the radicals that are most amenable to direct studies since experiments on the bond breaking reactions of a stable molecule with known thermochemistry can yield an activation energy which is directly relatable to the heat of formation of the radical in question. Experimental determination of the thermodynamic properties, particularly the heats of formation of unstable compounds such as H_2CNNO_2, represents a research frontier. Advances in the present context will have implications in many other areas. For larger species the logical approach is to use group additivity. There is, however, considerable uncertainty regarding group values for the nitramines. Here, the earlier recommendation regarding a systematic experimental and theoretical effort on determining the thermodynamic properties of a variety of propellants can be very useful.

3.5 Model Upgrades

The advent of high speed digital computers and the development of efficient computational algorithms have been essential in the modeling of gas phase combustion systems. The procedure used in the development of kinetic mechanisms for these flames provides a natural analog for the development of corresponding mechanisms for solid propellants. Kinetic mechanisms for hydrocarbon combustion, for example, have developed in a systematic way. Ignition studies in combination with shock tube data, premixed flame models in combination with temperature, species and flame speed measurements and counterflow models in combination with temperature, species, velocity and extinction measurements have enabled combustion scientists to refine their mechanisms to the point where they are applicable in a variety of physical configurations.

The rationale behind such an approach is that ultimately the models can be applied in realistic multidimensional systems in which there are complex fluid dynamic-thermochemical-kinetic interactions. The use of multi-dimensional systems as a vehicle for reaction mechanism development could produce an extremely inefficient research path. Nevertheless, multidimensional models are important and must ultimately be considered in a successful propellant modeling program.

Of primary importance is the fact that model development and associated experimental validation experiments must proceed together in a parallel manner. One logical development plan for key models and validating experiments is shown in Table 1. Further descriptions of the various modeling levels shown in Table 1 are presented below.

The work of Melius paralleled the first two steps used in gas phase combustion programs - zero-dimensional ignition[17] and one-dimensional premixed flame studies.[18] The next natural step that should be considered in the modeling of nitramine combustion is the analog of a counterflow flame. While such flames are important in turbulent combustion models, they are also one of the simplest configurations in which nontrivial fluid dynamical effects can be coupled with a system's thermochemistry. In gas phase combustion studies counterflow flames are produced using several different burners. In one case fuel is ejected through a porous cylinder into an on-coming stream of air. A thin flame sits above the surface of the cylinder. In another configuration two counterflowing, coaxial, concentric jets eject fuel and/or oxidizer. The result can be either a diffusion or a premixed flame. For solid propellants such a configuration can be achieved by counterburning two propellant strands with a small separation distance. Even though such a geometrical configuration is two-dimensional, an appropriate similarity solution exists in which the two-dimensional model can be converted into a one-dimensional problem along the stagnation point streamline. In this type of model the equations of mass and momentum are coupled with the energy and species equations. Although the final model is one-dimensional, nontrivial fluid dynamical effects can be included in the

Table 1 - Suggested Macroscopic Model Development Hierarchy and Validating Experiments

Model	Model Formulation	Combustion Parameter	Validation Experiment(s)
Gas Phase Ignition	0-dimensional	Kinetics	Shock tube Static reactor Flow reactor
Premixed Flame	1-dimensional boundary value problem	Kinetics, Burning rate	Strand burner, Flat flame burner
Counterflow Flame	1-dimensional boundary value problem	Extinction, Fluid/thermo coupling	Counterflow strand burner
Forced Ignition	1-dimensional parabolic	Minimum ignition energy	Strand burner
Heterogeneous Burn	2-dimensional parabolic	Multidimensional burning rate	Heterogeneous strand burner
Heterogeneous Burn with Cross Flow	2-dimensional parabolic	Propellant instability	Heterogeneous strand burner with axial flow

system so that extinction and the effects of stretch on both the primary and secondary flames can be studied. In addition, by counterburning a propellant and a binder one can simulate a counterflowing diffusion flame. Each of these configurations are feasible from both an experimental and a computational viewpoint and should be studied in detail. Moreover, the computational algorithms employed by Melius can be modified to enable the researcher to model such systems.

While one-dimensional models are important, they cannot provide all of the information that one needs in the evaluation of the performance of an energetic material. Multidimensional effects must ultimately be investigated. In particular, the burning of a composite propellant both with and without cross flow requires a multidimensional model. Such models could provide essential information on multidimensional burn rates and propellant stability. It is a common belief that combustion instabilities in solid propellant propulsion systems owe their existence to the interaction between fluid motion and combustion processes in a very thin region (of the order of 100 microns) adjacent to the solid surface. The fundamental concept underlying this belief is the recognition that energy will be fed into the acoustic mode when the fluctuating burning velocity (expressed often in terms of the varying mass flux) has a component in phase with the fluctuating pressure at the propellant surface. Its dependence on the fluctuating pressure is usually characterized by an admittance function whose dependence on fluid motion is not well understood. The central questions in a study of the velocity coupling effect on the unsteady burning of a solid propellant are:

1. What is going on near the surface of the burning propellant?
2. How does an oscillatory velocity parallel to the surface induce a fluctuating change in the burning rate and what is their relative phase relationship?

The detailed modeling of this system requires the coupling of the gas and the solid-phase solutions. As Culick points out, an accurate treatment of the gas-phase system is by far the most complex part of the modeling process.[71] In the solid phase the conservation of mass and momentum follows trivially and one reduces the problem to the conservation of energy. Although one can make a number of simplifying assumptions about the form of the transport laws, the complexity of the chemistry, and the level of coupling between the fluid dynamical and thermochemistry solution fields, it is our belief that detailed transport and multistep kinetics must ultimately be included in a complete gas-phase model.

A natural starting point in modeling such systems is the observation that the burning of a heterogeneous propellant has features that resemble both a premixed flame and a diffusion flame.[72] The burning rate in a diffusion flame is controlled by the rate at which the fuel and the oxidizer are brought together in stoichiometric proportion while in a premixed flame the burning rate is controlled by chemical reactions. Premixed flames can burn under lean, stoichiometric and rich conditions. We anticipate that the gases emerging from the surface of the propellant through pyrolysis will form a premixed fuel and oxidizer mixture with a spatially dependent equivalence ratio. The mixture will range from very lean to very rich in composition. Hence, a natural starting point in building a model that will predict the velocity coupling effects in the unsteady burning of a heterogeneous propellant is to consider a model that will predict the laminar burning velocity in a two-dimensional domain in which the incoming gases (e.g., the gases emerging from the propellant surface through pyrolysis) have an equivalence ratio that is spatially dependent. If the surface of the propellant is subjected to a parallel shear flow, then one can also attempt to simulate the burning of the periodic fuel-oxidizer structure of a heterogeneous propellant subjected to a tangential cross flow.

From a computational viewpoint, one-dimensional algorithms for solving the appropriate conservation equations are well established. Multidimensional algorithms are in a much less sophisticated state of development. Work is needed 1) in improving the efficiency of algorithms that solve sparse nonlinear equations, 2) in developing multidimensional adaptive mesh refinement algorithms, and 3) in developing parallel solution algorithms for the next generation of multitasking supercomputers.

3.6 Model Reduction and Lumping

At the current time, the coupling of detailed transport and finite rate kinetics in a multidimensional fluid dynamic-thermochemical propellant model are at the limit of computational feasibility on existing serial or vector machines. While a few computational studies could be performed with extensive computational resources, detailed parameter studies are computationaly infeasible. Modifications to the detailed model are required. Rather than start with a detailed description of the chemistry and transport, one can employ a reduced kinetics/transport approach.

Most complex combustion systems involve large numbers of chemical species. These species are related through a detailed kinetics mechanism involving many elementary chemical reactions. Solution of the governing equations in such systems reduces to the solution of an ordinary or partial differential equation for each species mass fraction. In some applications the determination of the appropriate chemical reactions and their respective rate constants can be a difficult task. It can be made simpler, however, by postulating a single global reaction for the system. This can also be useful when the size of the system to be solved (for the computer being used) results in a computationally infeasible problem. We realize, of course, that a global reaction mechanism does not provide detailed information on the system's minor species - information that is often needed in assessing the detailed structure of a reacting system. Determination of overall, global, reaction rates for flames has been investigated, for example, by Levy and Weinberg,[73,74] Westbrook and Dryer[75] and Coffee, Kotlar, and Miller.[76] In particular, one can use the detailed chemistry and the one-dimensional calculated temperature profile to obtain a heat release profile as a function of the independent spatial coordinate. Reaction rate parameters can then be obtained by a two parameter least squares fit to the data. Although such "empirical" approaches to lumping can be useful, it is clear that more systematic and rigorous techniques would be valuable. Such developments are discussed below.

The iterative research consisting of modeling and experiment which is a central thesis of this document aims to produce an overall comprehensive chemical and transport data base for nitramine decomposition. Inevitably, the model coming from this effort will be quite complex, involving many chemical components, perhaps in different phases, as well as a multitude of connecting physical parameters. Studies such as this ultimately aim to feed the engineering design process which will take into account further large scale dynamical processes. These latter processes with their own high level of complexity strongly motivate the need for model reduction or lumping of the microscopic results into their essence for practical exploitation at the engineering design level.[77]

Although this latter goal seems clear, the need for model reduction in fact occurs at all levels of the hierarchical flow in Figure 2. For example, to consider seriously a dynamical approach to unimolecular decomposition of complex polyatomic molecules will require an identification of the critical degrees of freedom as well as the lumping or projecting out of those with less importance.

Two general issues arise here: (1) system reduction, and (2) system lumping. By system reduction we refer to the process of identifying critical parameters and eliminating those of lesser importance. The parameter sensitivity coefficients $\partial O_i/\partial \alpha_j$ provide direct information bearing on system reduction, where O_i is the i-th physical observable and α_j is the j-th system parameter (Section 4 will further discuss the meaning of these coefficients). For example, the larger parameter sensitivities of key dependent variables would indicate which parameters should be retained and in an iterative fashion the model would be rerun accordingly for its validation. Model reduction can result in some degree of computational savings, but its chief importance lies in the physical insight gained and reduction of a model to its physical essence. A critical point to understand is that the form of a reduced model will likely depend on what observable characteristics are considered significant.

System lumping has the potential for much more significant computational savings and the optimal route to achieve lumping will require considerable exploratory research. Traditionally, lumping is often done in many fields by routine pairing of system dependent variables based on physical insight or other like indicators. In the case of kinetics, steady state or equilibrium approximations are often invoked to replace more complex differential equations by simpler algebraic relationships among the chemical species. In extreme cases, one might also justify reducing the entire chemical kinetics mechanism to an effective heat release rate as mentioned above. Clearly, more systematic means for lumping are necessary, whether they be performed on kinetic mechanisms or the degrees of freedom in a molecule undergoing unimolecular dissociation.

Although no definitive approaches to system lumping now exist, three viable avenues of current approach can be identified.

1. Scaling and Self Similarity of Strongly Coupled Systems As an Indicator of Lumping. An increasing body of computational sensitivity analysis evidence has shown that system collapse can occur in chemical kinetics when the species or general dependent variables are sufficiently strongly coupled. The variables thus act in concert immediately suggesting that a reduction in their number could be achieved. It remains for further research to exploit the sensitivity coefficients, $\partial O_i/\partial \alpha_j$, to produce lumped models.

2. System Lumping via Linear Transformation.[77] Prior literature in chemical engineering dating back a number of years has considered formal lumping of chemical kinetics through linear transformations of the following form:

   $\boldsymbol{\mathit{O}} = \mathbb{M}\,\mathbf{O}$ where $\mathbb{M}$ is a rectangular lumping matrix connecting the original dependent variable vector $\mathbf{O}$ of dimension n with its lumped counterpart $\boldsymbol{\mathit{O}}$ of dimension n' where $n' < n$. Recent research has been directed towards identifying the necessary and sufficient conditions for $\mathbb{M}$ to exist and produce exact lumping.[78] Although exact chemical kinetic lumping is certainly likely to be the exception rather than the rule, the establishment of formally exact lumping criteria can form the basis for seeking approximate lumping schemes in a controlled fashion. An important point to understand is that even the relatively simple case of lumping by linear transformation will produce a nonlinear mapping of the actual differential equations to a reduced set of dimension n'. This seems to be a very promising line of research which should have equally direct applications to molecular dynamics since this latter problem may be expressed in exactly analogous mathematical form.

3. Lumping By Nonlinear Transformation. The direct generalization of Item 2 above is to the consideration of nonlinear transformations for system lumping. There is no existing general formulation for this approach, but a promising avenue of study appears to be through the consideration of Lie transformations.[79] Again, although the generator of a Lie transformation is linear, its exploitation to move through the hyperspace of all system variables can be highly nonlinear. In its current stage of development, this approach seems to hold longer range prospects for reaching fruition, and it may ultimately lead to a wider degree of applicability.

Research on lumping and system reduction will clearly have an important impact on the practical utility of the energetic materials research. Furthermore, may important spin-offs will result since exactly the same techniques have application in a host of allied areas.

4. RESEARCH DIRECTIONS FOR CRITICAL COMBUSTION AND SUPPORTING LABORATORY EXPERIMENTS

4.1 Macroscale Combustion Experiments

4.1.1 Goals

Macroscopic parameters of propellant combustion, such as the burning rates, are already being measured as a function of pressure and initial sample temperature in several laboratories.[80] Kinetic isotope effects have even been observed in the rate of thermal decomposition of RDX and HMX[81] and in their burning rates.[82] Such observations clearly have implications for the mechanisms of decomposition and combustion. For a deeper understanding of the underlying chemical and physical processes governing nitramine propellant combustion, it is clearly important to measure such parameters as burning velocities, species concentrations, temperature, and density in nitramine and nitramine/binder flames. Aside from providing an experimental characterization of the system, these data will provide specific information with which chemical kinetic flame models can be compared.

4.1.2 Facilities and Techniques

Because the surface of a solid propellant regresses during combustion, the optimal use of most diagnostic techniques will require a means to maintain the probe at specific positions with respect to the burning surface. For this purpose, strand burners have been developed in several laboratories. An example of such a device is illustrated in Figure 6. Here a motor is used to translate a strand of burning propellant so as to maintain the burning surface in a fixed spatial position. Several ports are included in the burner, whose total pressure can also be varied, to allow for optical probes. Thus far, burners have been used to take high-speed photographs (both normal and schlieren) to visualize the macroscopic phenomena and to visualize the gas flow field. From the standpoint of simulating opposed flow dynamics (see Subsection 3.5) a burner with two opposing strand feeders such as that shown in Figure 6 is especially useful.

Species and temperature profiles in actual nitramine propellant flames can be used as test data for model calculations. Thus, recent mass spectroscopic measurements on RDX flames[83] are very important and more such experiments need to be done. However, the chemistry model can also be tested by considering subsets of chemical reactions under controlled experimental conditions. In particular, shock tubes, flat flame burners, flow reactors, and static reactor cells can all provide valuable experimental data upon which to test the chemical models. These experiments should be done in conjunction with the modeling using sensitivity analysis to help verify the chemical models.

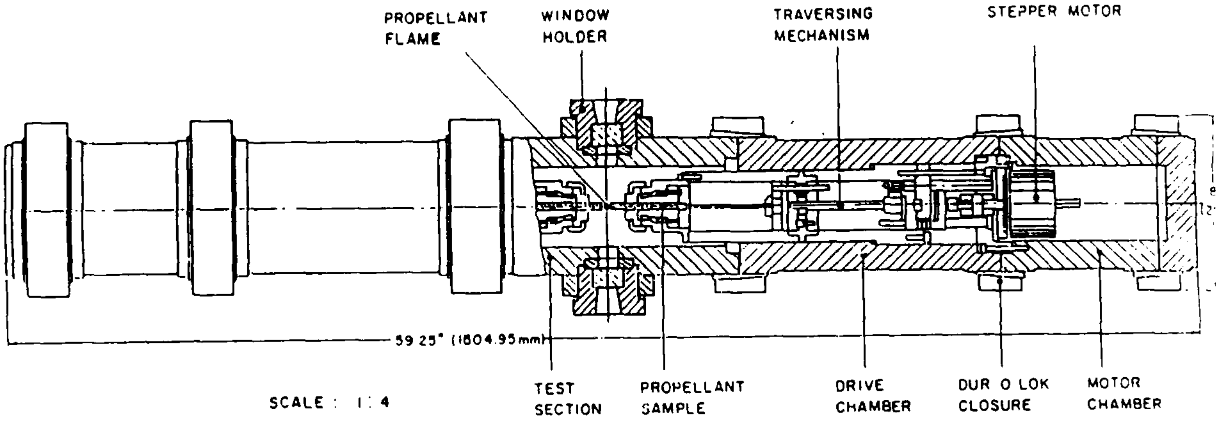

Figure 6. Schematic Diagram of a Double-Ended Windowed Strand Burner Used in the Laboratory of Prof. K. K. Kuo.

In addition to actual combustion experiments, a large number of studies involving the pyrolysis of both neat nitramine compounds and formulated nitramine propellant mixes will be necessary in order to understand and model decomposition and ignition properties and mechanisms. In addition to traditional thermogravimetric studies, high heating rate experiments involving laser heating of bulk samples and shock tube or hot drop tube heating of smaller particulate samples will, when properly coupled to the advanced diagnostics discussed below, yield valuable data on both condensed phase transformations and their gas phase products. A key goal of all such experiments will be to assess whether the condensed phase physical and chemical processes postulated in Figure 1 have a major role in determining the identity of the initial gas phase products as well as the rate of ignition and burning processes.

4.1.3 Diagnostics

Whichever type of combustion or kinetic facility is used to generate target combustion mixtures, the utility of such measurements is strongly dependent on the quality of the diagnostics arrayed to gather the required data. Continual improvement in diagnostic capabilities is a hallmark of recent physicochemical research, and key diagnostic advances are reviewed below.

4.1.3.1 Temperature

The most important single measurement which can be made of the flame is the temperature distribution. Availability of this information would significantly constrain and simplify the theoretical kinetic modeling efforts described in Section 3. In addition, this would allow a more realistic assessment of the importance of condensed phase chemistry in the propellant combustion process.

Thus far, temperature has been measured in the solid by imbedding miniature thermocouples within propellant strands and following the temperature within the strand as the solid heats up through the flame until the probe is destroyed.[84] A significant uncertainty in these studies is the location of the burning surface during the heating process. This is usually taken as an inflection point in the heating curve. While thermocouples are essentially the only technique thus far applicable to the measurement of the temperature of the solid, it is clearly important to measure the temperature throughout the gas-phase flame.

Molecular spectroscopy finds great use as a diagnostic in macroscale combustion experiments, as well as in supporting laboratory experiments for the identification of intermediates and the measurement of kinetic parameters of elementary reaction steps. The uses of molecular spectroscopy are discussed in greater detail in Section 4.2.2. There are several spectroscopic diagnostic methods available for the determination of flame temperature profiles. Coherent anti-Stokes Raman spectroscopy (CARS)[85,86] appears to be the best approach for the determination of the temperature (as well as the concentration of a number of the major stable chemical species) in the gas above burning solid propellants. Coherent optical methods offer significant advantages, such as increased signal strength and spatial resolution, over incoherent techniques. In this method, the temperature is determined from an analysis of the profile of the rovibrational band of a detected molecular species. This is analogous to the measurement of temperature through determination of rovibrational populations by visible laser-induced fluorescence or infrared absorption.

The CARS technique has already been used for temperature and species measurements in augmented engine exhausts.[87] Typical spatial resolution with CARS in laboratory flames is a cylindrical zone approximately 100 microns diameter by 1 mm long. It should be possible to reduce the diameter to 50 microns or less, which would provide spatial resolution adequate to study the dark and secondary flames zones of a burning propellant at about 20 atm.[88] In its usual application, CARS is designed to probe a single point at the focus of the two laser beams. It would be interesting to be able to probe more than one point simultaneously. Such a capability has been demonstrated with CARS using slit-shaped laser beams.[89] There are also a number of other approaches possible with CARS which would allow such capabilities as simultaneous species measurements, self-calibration, etc. In view of the demonstrated utility of CARS as a combustion diagnostic, it is important that it be further developed and applied specifically to nitramine combustion.

4.1.3.2 Combustion Species Diagnostics

Gas sampling techniques have traditionally been used to observe stable species in a propellant flame.[90] The quantitative interpretation of these early experiments is suspect. Mass spectrometric sampling has more recently been used to determine stable species concentrations as a function of distance in several propellant flames.[83] It is clearly useful to carry out more mass spectrometric probe sampling studies of propellant burning. With molecular beam sampling techniques, it should also be possible to detect labile species.

One significant uncertainty in the interpretation of mass spectral data is the origin of the observed mass peaks, i.e., whether these are parent or daughter ions. The application of different ionization methods is clearly important in resolving such ambiguities. An example of the utility of such approaches is the recent chemical ionization study of the pyrolysis of RDX by Snyder et al.[91] The use of the gentle chemical ionization technique, as well as isotopic labelling of the RDX, allowed determination of the chemical formulas for the observed pyrolysis features. The coupling of molecular beam sampling with laser pumped resonance enhanced multiphoton ionization (REMPI, discussed below) and mass selective detection may prove to be an important novel species diagnostic system.

Simultaneous thermogravimetric modulated beam mass spectrometry and time-of-flight (TOF) velocity analysis has also been employed to study the thermal decomposition of HMX and RDX.[92] In this case, the molecular weight of the fragment associated with a given ion mass peak is approximately determined by TOF velocity analysis from the effusive source. The mass loss observed by a microbalance is then correlated with the fragment deduced from the TOF mass spectra. One drawback of such techniques is that the propellant decomposition must be carried out sufficiently slowly so that the pressure of the decomposition products above the sample remains low, conditions quite different than for actual burning of a propellant.

Electronic emission spectroscopy has also been employed and a number of radical species have been seen.[93-95] However, this method suffers from the fact that the signal is an integral over the line of sight; hence, it does not have high spatial resolution. A more fundamental difficulty with using electronic emission spectroscopy as a flame diagnostic is that the visible chemiluminescence from chemical reactions is usually a small fraction of the total reactive flux.[96] Nevertheless, this technique can provide useful information about the spatial distribution of specific free radicals within the propellant flame, provided the excited state emission reasonably tracks the production of the ground state electronic state, as appears to be the case for CN in laboratory flow systems.[97] The use of modern FTIR is a promising method of using spontaneous flame emission to gain information on the flame chemistry, because emission from vibrationally excited molecules would be much more diagnostic of the flame chemistry.[98,99]

Infrared absorption was employed a number of years ago to probe propellant flames.[100] Absorption spectroscopy suffers from the fact that it is a line of sight method and has poor spatial resolution. Modern FTIR absorption methods have, in fact, found considerable use in thermal decomposition studies of propellants. Brill and co-workers have used this technique to investigate changes in molecular structure accompanying phase transitions in RDX.[101] In addition, rapid scan FTIR spectroscopy has enabled the study of the pyrolysis of energetic materials under fast heating conditions.[102]

Considerable progress has been made toward the development of fast-response nonintrusive laser diagnostic probes suitable for the detailed study of the mechanism of nitramine propellant combustion.[103-105] It is clearly important to apply these methods to probe the flame structure and concentration profiles adjacent to burning solid propellants. The CARS technique, previously discussed in terms of flame temperature measurements, can provide concentrations of selected major species.

The laser-induced fluorescence technique has been shown to be a very sensitive method for the determination of concentrations of a number of molecules, principally diatomic and triatomic free radicals, in combustion environments.[106-108] As discussed in more detail in Section 4.2.6, there are sufficient spectroscopic data available (wavelengths, band strengths, radiative lifetimes, etc.) to design and interpret experiments for concentration measurements of most diatomic radicals likely to be of importance (e.g., OH, CN, NH) There are a number of polyatomic species of importance in nitramine decomposition for which the laser fluorescence technique is applicable. These are discussed in Section 4.2.3, and their status with respect to in situ detection briefly reviewed.

Because of the high pressure of the nitramine combustion environment, it is necessary to take account of collisional effects, as has been recognized for some time. Quenching of the electronically excited state is the principal collisional perturbation. Considerable effort has been made to measure quenching rate constants by a variety of potential collision partners and as a function of temperature. Quenching, of course, has the effect of reducing the fluorescence quantum efficiency, which must be known to determine absolute concentrations. Even if only the relative concentration of a given species as a function of position were desired, the fluorescence intensity may not accurately reflect the concentration profile because of the variation of gas composition through the flame. Garland and Crosley[109] have recently surveyed the current knowledge on the quenching of electronically excited states of OH, NH, and CH, as it pertains to combustion diagnostic studies. For OH, the total quenching rate can be calculated to an accuracy of perhaps ±30% for typical flames. Moreover, perhaps fortuitously, the total OH(A) quenching rate varies by only 30-50% through the flame for a variety of exemplary flames. There is at present insufficient information available to make similar estimates for NH or CH. If narrowband detection of the fluorescence intensity is employed, say for reduction of scattered light or flame emission, collisional energy transfer within the electronically excited state must also be taken into account.[28]

Saturated fluorescence,[110-112] in which a high laser power density is employed to cause stimulated emission to be the dominant excited state removal path, is an alternative method to avoid the problem of quenching. While this technique has attractions, it is not applicable or necessarily easily interpretable under all circumstances.

One particularly promising innovation for the application of laser diagnostics to combustion studies is the use of planar imaging techniques.[113] This allows the determination of a "snapshot" of the concentration profile through a plane. Planar laser-induced fluorescence signals have recently been observed for OH and CN in a flame above a solid propellant at 0.5 MPa.[104] Because of the previously mentioned quenching problem, the conversion of these signals to concentration profiles is nontrivial. It is important for such measurements to be continued and refined. Of special significance would be the determination of absolute concentrations of several species as a function of position within the flame,[114] in order to provide maximal information for comparison with flame models.

Resonance enhanced multiphoton ionization (REMPI) has also been successfully used for the detection of several species of combustion relevance, including H, O, CH_3, and HCO, in both laboratory spectroscopic experiments and in flames.[115-118] This technique may also find use in the study of nitramine combustion. However, one drawback, at least for studies at high pressures, is the necessity for insertion of an ion-collecting probe into the system. Alternatively, as noted earlier, a neutral molecular beam can be sampled and REMPI used as a selective ionization procedure for mass spectrometric detection.

The combustion community has had considerable interest in the development of multiphoton excitation schemes for the detection of light atoms in combustion environments.[119] Two different approaches have been taken, namely observation of the fluorescence emission from the multiphoton resonant excited state[119-122] and absorption of an additional photon to produce ionization,[115,116] as discussed in the previous paragraph. The former method has advantages over the latter in that it does not require the insertion of a probe into the medium and can be used to obtain two-dimensional images of atomic concentrations in flames, as has been recently demonstrated.[120,121] These multiphoton techniques will find use in the determination of profiles of atomic concentrations in nitramine flames. Again, collisional effects will need to be considered in reducing signals to concentrations.[116,119,122,123]

4.2 Supporting Laboratory Experiments

4.2.1 Goals: Reaction Rates, Diagnostics Support

The first stage in the decomposition of the initial gas phase species in a nitramine flame may occur on a time scale as short as nanoseconds, and, at a pressure of 1 atmosphere, each subsequent stage in the decomposition process takes place on a time scale ranging from nanoseconds to microseconds. This latter time scale is compressed at higher pressures. Many reaction intermediates are formed and consumed on the time scale of typical observations, so it is crucial to evaluate the presence of key reaction intermediates by direct observation.

While the spectral techniques discussed in Section 4.1 are currently applicable primarily to small (1 to 3 atom) species, diagnostics for the positive identification of polyatomic reaction intermediates are in the early development stages. As these techniques evolve, it will become possible to study the elementary reaction chemistry of species identified from kinetic models as probable key intermediates in the decomposition of nitramine propellants. A prime example of these species is the H_2CN molecule, which has been suggested as a likely key intermediate but whose elementary reaction chemistry is at present completely unknown.

The following two Subsections (4.2.2 and 4.2.3) discuss the basic spectroscopic studies required to develop the non-intrusive spectral probes needed both for reactive species monitoring in nitramine combustion studies and laboratory determinations of specific kinetics measurements. Subsection 4.2.4 also deals with species diagnostic development, focusing on sampling-based techniques. Subsection 4.2.5 reviews the types of kinetic experiments needed to gather the reaction rate parameters required by the kinetic ignition and combustion models discussed in Section 3. Finally, Subsection 4.2.6 reviews the evaluated spectral data bases available for diagnostic selection and design.

4.2.2 Experiments Supporting Spectroscopic Diagnostic Development

Molecular spectroscopy is often the method of choice for both combustion and kinetic studies. It is a nonintrusive technique and is especially well suited to the distinction between isomeric species. On the low energy scale, it can, for example, readily distinguish between stereoisomers such as cis- and trans-HONO. It also provides an excellent means of distinguishing between species which have the same molecular formulas but different chemical bonding structures,such as HNCO, HCNO, and HOCN, all of which may play important roles in nitramine reaction systems. Modern laser systems afford the great advantage of high detection sensitivity coupled with space and time selectivity.

Conventional absorption and emission spectroscopy have been very useful in elucidating the spectra of diatomic reaction intermediates, such as OH, NH, and CN. The flash photolysis technique has found considerable use for the observation of electronic absorption spectra of many small polyatomic reaction intermediates, such as HNO,[124] NCO,[125] and H_2CN.[126] The usefulness of flash photolysis coupled with spectroscopic detection is limited to species which have relatively intense electronic absorptions in the visible-ultraviolet-vacuum ultraviolet spectral regions. If the band system is diffuse - as for H_2CN - the technique may still be useful, but structural information, crucial for the positive identification of the reaction intermediate, may be lost.

The matrix isolation technique provides a powerful tool for obtaining survey spectra of chemical reaction intermediates over the entire infrared and visible-ultraviolet region. Concentrations of free radicals as high as a few tenths of a percent have been stabilized in the inert matrix material. Ground state vibrational absorptions of covalently bonded species typically lie within 1% of gas-phase band centers for argon matrices; the deviations from gas-phase values are even smaller for neon matrices.[127] Electronic band origins of covalently bound species isolated in argon and neon matrices are usually within about 2% and 1%, respectively, of their gas-phase frequencies.[128] Therefore, species identifications in the environment of an argon or neon matrix can provide a valuable guide for the gas-phase laser studies.

Since molecules are stabilized in their ground states at the 4-14 K temperatures used for matrix studies, possible spectral complications due to hot bands are eliminated. A "map" of the transitions arising from the molecular ground vibronic states is thus provided. Recent matrix observations[129] of the electronic spectrum of H_2CN excluded a possible hot band contribution to the previously reported gas-phase spectrum.[126] Elimination of the hot band assignment is important to the extrapolation of the spectral data to high temperature environments. Matrix studies of the previously unreported near-infrared electronic transition of HCC,[130] expected to be an important intermediate in binder degradation, revealed a wealth of structure connected with extensive perturbations by highly excited ground-state vibrational energy levels.

Lasers have proved to be extremely valuable in the detection of chemical reaction intermediates in the gas phase and in the development of spatial diagnostics of these species. Presently available laser-based detection techniques span the spectral range from the far infrared to the vacuum ultraviolet. The most commonly used and one of the most sensitive involves fluorescence excitation with dye lasers or their frequency-doubled radiation. This method is limited to species which have reasonably intense fluorescence spectra, i.e., diatomics and certain small polyatomics. Nevertheless, laser fluorescence detection has seen considerable use as a spectral diagnostic, as discussed in Section 4.1.3.2. The availability of tunable infrared lasers, including color center lasers, laser difference frequency spectrometers, and tunable diode lasers, opens up the possibility of the more widely applicable detection of molecules by vibrational transitions.

Recent developments in digital electronics and in algorithms have resulted in wide application of Fourier transform infrared spectroscopy. The advantages inherent in Fourier transform data analysis have resulted in greatly improved signal-to-noise ratios even at much reduced observation times. Gas-phase infrared spectra have been obtained for a few reaction intermediates, including CH_2NH,[131] with Fourier transform (FTIR) detection systems.

4.2.3 Spectroscopic Diagnostics

Tables 2 and 3 summarize the status of the development of diagnostics for species which, according to present models, should play key roles in nitramine ignition and combustion. Table 2 focuses on relatively small nitramine reaction intermediates which can be monitored with available or relatively easily envisioned spectral techniques. Only for stable molecules, such as NO and NO_2, and for a few diatomic free radicals is diagnostic development far advanced. Indeed, the spectra of several small polyatomic species which play important roles in the models have yet to be observed; Table 3 lists a number of the small polyatomic species currently believed to play a critical role in nitramine combustion. Some of the problems in developing diagnostics for these species will be considered in the following discussion.

Table 2 - High Priority Reaction Intermediates for In Situ Nitramine Flame Diagnostic Development

Species	Spectral Region	Possible Diagnostics	Status[a]	Comments
CN	380-390 nm	LIF	Lifetime	Much development
NH	330-340 nm	LIF	Lifetime	Much development
NO	224-226 nm	LIF	Lifetime	Much development
NO_2	Visible	LIF	Lifetime	Much development
NCO	450-550 nm	LIF	Lifetime	Some development[b]
HNO	700-800 nm	LIF	Lifetime[c]	
	1560 cm^{-1}	IR laser	Spectrum[d]	
HONO	800-900 cm^{-1} 1200-1300 cm^{-1} 1650-1750 cm^{-1}	IR laser	Spectrum[e]	2-laser UV detection possible[f]

[a] Status with respect to quantitative use in flames.

[b] Copeland, R.A., Crosley, D.R., and Smith, G.P., Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1985, pp. 1195-1203; Wong, K.H., Anderson, W.R. Kotlar, A.J., and Vanderhoff, J.A., J. Chem. Phys. 81:2970-2974 (1984).

[c] Dixon, R.N., Noble, M., Taylor, C.A., and Delhoume, M., Faraday Discuss. Chem. Soc. 71:125-142 (1981); Obi, K., Matsumi, Y., Takeda, Y., Mayama, S., Watanabe, H., and Tsuchiya, S., Chem. Phys. Lett. 95:520-524 (1983).

[d] Johns, J.W.C., and McKellar, A.R.W., J. Chem. Phys. 66:1217-1224 (1977).

[e] Kagann, R.H. and Maki, A.G., J. Quant. Spectrosc. Radiat. Transfer 30:37-44 (1983); Maki, A.G. and Sams, R.L., J. Mol. Structure 100:215-221 (1983); Maki, A.G., J. Molec. Spectrosc. 127:104-111 (1988).

[f] Radhakrishnan, G., Parr, T., and Wittig, C., Chem. Phys. Lett. 111:25-32 (1984); Vasudev, R., Zare, R.N., Dixon, and R.N., J. Chem. Phys. 80:4863-4878 (1984).

Where spectra have yet to be obtained, it may be advantagous first to search for absorptions using the matrix isolation technique, since the molecules of interest are expected to have short lifetimes against chemical reaction in the gas phase. Isotopic substitution experiments will aid in the positive identification of the infrared spectra of these species, and the identification of visible-ultraviolet bands which behave similarly under different preparative and photolysis conditions will aid in the assignment of electronic transitions of these species. It is anticipated that low-lying transitions of several of these molecules, like those of closely related species, may be dissociative or strongly predissociated. Therefore, it is suggested that diagnostic development based on infrared laser absorptions may be appropriate.

Table 3 - High Priority Reaction Intermediates for Reaction Mechanism Diagnostic Development

Species	Spectral Region	Possible Diagnostics	Status	Comments
H_2CN	280 nm	UV Absorption	Spectrum	All bands diffuse
H_2CNO		IR?	No data	
HNCO		IR Laser	Spectrum	
HCNO		IR Laser	Spectrum	
HOCN	1080 cm^{-1}	IR Laser	Spectrum	Matrix isolation[a]
	2300 cm^{-1}	IR Laser	Spectrum	Matrix isolation[a]
	3600 cm^{-1}	IR Laser	Spectrum	Matrix isolation[a]
HONC	1230 cm^{-1}	IR	Spectrum	Matrix isolation[b]
	3440 cm^{-1}	IR	Spectrum	Matrix isolation[b]
HNOH		IR?	No data	Microwave detection?
H_2NO		IR?		Far IR-LMR detection[c]

[a] Jacox, M.E. and Milligan, D.E., J. Chem. Phys. 40:2457-2460 (1964); Bondybey, V.E., English, J.H., Mathews, C.W., and Contolini, R.J., J. Molec. Spectrosc. 92:431-442 (1982).

[b] Maier, G., Teles, J.H., Hess, Jr., B.A., and Schaad, L.J., Angew. Chem. 100: 1014-1015 (1988), Angew. Chem. Int. Ed. Engl. 27:938-939 (1988).

[c] Davies, P.B., Dransfeld, P., Temps, F., and Wagner, H.G., Ber. Max-Planck-Inst. Stromungsforsch. no. 6:1-25 (1984); J. Chem. Phys. 81:3763-3765 (1984).

Quantitative species identification is possible for the stable molecules listed in Table 2, but will be very difficult to achieve for the more reactive or less stable species. It is rarely possible to obtain complete conversion of a stable species of known concentration to a transient product. However, the determination of relative concentrations of transient species is still useful in kinetic studies of elementary reactions.

Infrared detection of transient molecules in the gas phase has been employed in only a few kinetic studies.[132,133] At the high resolution of infrared diode lasers, individual rotational transitions are prominent. As the system pressure is increased, these lines are broadened, and the detection sensitivity is decreased. Therefore, infrared lasers are best suited to measurements at low total pressures. As the temperature is raised, the complexity of the spectrum will increase. For low molecular weight species such as those of formula NH_2O, it may be feasible to extend the detection technique to somewhat higher temperatures.

In some special cases, it may still be possible to utilize visible or ultraviolet laser fluorescence for the detection in kinetic studies of species with dissociative or predissociative excited states. The HONO molecule was successfully detected in the ultraviolet photodissociation of nitropropane by a 2-step laser technique involving first the photodissociation of HONO and then laser fluorescence detection of the OH fragment.[134] Unfortunately, quantitative detection of HONO will be difficult, and the sensitivity of this method is limited by the presence of OH produced by processes other than HONO photodissociation.

4.2.4 Other Diagnostics

Other detection techniques besides electronic or vibrational spectroscopy have been employed to observe intermediates in the decomposition of nitramines. The best example of this is the electron spin resonance (ESR) study of Beyer and Morgan.[135] This technique was used to detect several free radical species in the effluent from the slow pyrolysis of RDX and HMX. In particular, they were able to observe the important H_2CN radical, as well as NO_2. However, ESR does not have the sensitivity or spatial resolution required for in situ studies of nitramine combustion.

Another potential diagnostic, particularly for supporting kinetic studies, is resonance enhanced multiphoton ionization (REMPI) which was briefly mentioned in Section 4.1.3.2. This technique has become an important laser spectroscopic technique for studying transient free radicals because it offers the advantage of excellent sensitivity, even for radicals not suitably detected using laser induced fluorescence (LIF), Raman, or coherent antistokes Raman (CARS) spectroscopies. Although relatively new, its contributions to free radical spectroscopy are already significant. At present, REMPI can sensitively detect over 41 free radicals,[136] many of which cannot be sensitively detected by any other optical method. REMPI spectroscopy has provided a first view of the electronic spectra of ten radicals (e.g., CH_2OH, SiH_3, GeH_3...) and has doubled or tripled the spectroscopic data of others (e.g., CH_3, HCO, CH_3O...).

Finally, various forms of advanced mass spectroscopy (with or without REMPI detection) including molecular beam sampling and Fourier transform mass spectroscopy based on ion cyclotron resonance techniques may also play a key diagnostic role, especially for kinetic studies of large molecules.

4.2.5 Kinetic Techniques and Experiments

There is a critical need for the measurement of reaction rate constants and the determination of product branching ratios. These are required for the development of a realistic kinetic model to describe nitramine combustion. While the measurement of rate constants is clearly significant, it is also necessary to have estimates of branching ratios for a number of reactions since the product branching can determine the actual mechanism of decomposition. It is considerably more difficult to determine branching ratios, as opposed to rate constants, since the former requires measurements of ratios of concentrations (either of a product vs. reactant or of two products) while the latter can usually form the time dependence of the concentration of a single species (at least in the pseudo-first order regime).

Table 4 contains a summary of the commonly employed kinetic techniques that can be applied to the determination of gas phase mechanisms and rate constants for reactions such as listed in Figure 4. The shock tube[137] has unique capabilities for studying rates and mechanisms for unimolecular decompositions while the other methods are more suitable for

Table 4 - Gas Phase Kinetics Techniques

Technique	Temperature Range (K)	Pressure Range (atm)	Comments
Shock tube	300-10,000	0.1-1000	Short measurement duration
Fast-flow reaction	200-1800	0.001-1	Can pre-prepare many reactants at low pressure
Flash photolysis/ resonance fluorescence and absorption	200-1400	0.05-10	Limited to labile species produced by photolysis
Pulsed radiolysis	200-1400	0.05-100	Similar to Flash Photolysis /Resonance Fluorescence & Absorption
Crossed molecular beam or molecular beam/bottle	NA[a]	NA	Product branching ratios

[a] Collisional energy range 0.05-5 eV.

examining bimolecular processes.[138-140] This list is not meant to be exclusive. In earlier sections we have described contributions from static (bulb) and laser pyrolysis experiments. The real surprising feature is that so few kinetic experiments have been carried out that meet modern standards on the validity of such measurements.

The various bulb and flow methods have been extensively employed for the measurement of thermal rate constants of a wide variety of chemical reactions. Such experiments have given considerable insight into the reaction mechanism of the combustion of various species.[141] Recent advances in techniques have allowed for the study of elementary radical-radical reactions directly rather than by modeling of multistep mechanisms.[142] For a number of the elementary reactions of importance in nitramine combustion, the branching into the various possible chemically distinct pathways is unknown. For example, the present kinetic models of nitramine combustion (see Section 2.2) suggest that knowledge of the branching ratio for the reactions:

$$
\begin{aligned}
H_2CN + NO_2 \rightarrow H_2CNONO^*,\ H_2CNNO_2^* &\rightarrow H_2CNO + NO \\
&\rightarrow HONO + HCN \\
&\rightarrow HCHO + H_2O \\
&\rightarrow H_2CNNONO \\
&\rightarrow H_2CNNO_2
\end{aligned}
$$

is important in eliminating some of the uncertainties in the decomposition of intermediate nitramine decomposition species. This reaction is the prototype of the reaction of other radicals having H atoms, such as CH_3O, with NO_2. Thus, it would be important to have at least one example of a reaction system where the branching ratios are known.

The usual kinetic measurement provides only the total bimolecular rate constant. The measurement of product branching ratios presents a significantly greater challenge because of the necessity to calibrate detected reactant and product signals with respect to one another. The NH_2 + NO reaction, which is important in the formation of nitrogen oxides in various combustion and atmospheric processes, offers a good example of the problems in estimating branching ratios.[143]

In this regard, as illustrated by the study of Lee and co-workers on the infrared multiphoton dissociation of RDX,[21] molecular beam methods are clearly useful even though this technique does not easily yield total cross sections for reactive collisions. This technique can probe unimolecular decomposition channels which are of great importance for nitramine decomposition (see below). There are also problems with respect to the interpretation of the branching ratio information, since there are uncertainties regarding the energy distribution. It is somewhat surprising that, except for the molecular beam technique, none of the other well established methods have been directly applied to problems associated with propellant decomposition. In addition, molecular beam techniques can be used to investigate the dynamics of radical-radical reactions at high collision energies, corresponding to the high temperatures in the secondary flame.

For any type of reaction there is an optimum method and reaction condition for the determination of the desired information. As noted above the most important guarantee of reliable results is proper experimental design. It is our opinion that most of the reactions that may be important in modeling propellant combustion are to some degree accessible with currently available methodology. Probably the most difficult rate constants to measure are those involving polyatomic radical-radical interactions. This is coupled with the fact that rate constants for disproportionation reactions are most difficult to estimate. In order to carry out such experiments one must simultaneously generate and determine the concentration of two radicals, consider the possible interactions with other radicals that are present in the system, their unimolecular decomposition processes and ultimately a multiplicity of reaction channels.

An important problem in these studies will be the handling of nitramines and related compounds. They are in general of low volatility and stability and particularly subject to surface catalysis. For the latter, the shock tube offers special advantages since the short heating time and the gas dynamic nature of the heating assure the absence of surface processes. Nevertheless, this is a problem in experimental technique which can probably be solved with experience. We note that in the stratospheric chemistry area unstable compounds such as $ClONO_2$ and N_2O_5 are extensively studied.

The chemical complexity of nitramine propellants makes proper understanding of reaction mechanisms before the measurement of rate constants mandatory. The key to unambiguously determining mechanisms is the possibility of detecting as many products as possible. Unfortunately, for any given system nonintrusive spectroscopic techniques can detect one or at most a few species at any given time. This is in general insufficient for unambiguous determination of mechanism. Thus, we may face the necessity of intrusive probes and or the inference of mechanisms from final product analysis. This means the use of mass spectrometry or the various chromatographies. With the mechanism properly defined, then the application of nonintrusive spectroscopic techniques provides a means of fine tuning rate constant measurements. The ideal situation is undoubtedly the combination of intrusive and nonintrusive techniques. An example of a high temperature flow reactor equiped with a variety of nonintrusive spectral probes as well as molecular beam mass spectroscopic sampling is described in Reference 144.

It should be noted that the same diagnostics that have been discussed in an earlier section as possibilities for probing combustion species distributions can be utilized with probably a greater chance of success in kinetic studies inasmuch as such systems are intrinsically cleaner. Indeed, kinetic studies provide an excellent test bed for the validation of combustion species diagnostics.

The major focus of this subsection has been on techniques to gather the gas phase kinetic data which current nitramine combustion models clearly require.[17-19] If the pyrolysis experiments recommended in Subsection 4.1 show a critical need to more fully understand condensed phase or gas-surface kinetic processes, suitable experimental kinetics techniques involving condensed phases will have to be developed.

4.3 Evaluated Data Bases

The critical role of evaluated kinetic and thermochemical data bases in modeling was discussed extensively in Section 3; here we will briefly review spectroscopic data bases available for diagnostic evaluation and experimental design.

Several recent compilations give evaluated energy level data for a large number of small molecules. Huber and Herzberg[145] have provided an authoritative summary of spectroscopic constants for diatomic molecules. Earlier volumes by Herzberg are the basic reference to the theory of molecular electronic transitions[41] and vibrational-rotational spectra. [146]

For many years, the tables of spectral data for molecules which possess from 3 to 12 atoms which were included in the volume on electronic transitions of polyatomic molecules[41] were the prime source of spectroscopic data for stable molecules, free radical reaction intermediates, and the few small polyatomic molecules for which spectral data were then available. Although spectral data for stable molecules were quite well established at that time, the development of new techniques, already discussed, has vastly enlarged the literature on the molecular energy levels of polyatomic transient molecules since that time. To meet the need for critically evaluated ground-state vibrational energy levels for small polyatomic (3-16 atoms) transient molecules, defined as species which have lifetimes against chemical reaction which are too short for conventional spectral observation in a simple gas cell, a compilation has recently been published.[147] A second compilation, giving evaluated electronic spectral data for polyatomic transient molecules with from 3 to 6 atoms, has just appeared.[148] The tables in this latter compilation include electronic energy levels, vibrational spacings, principal rotational constants, and radiative lifetimes. Because the field is currently so active, the ground-state vibrational data for many of the transient molecules included in this compilation are significantly revised from the corresponding data in the 1984 tables. Recent additions to the ground-state vibrational energy level data available for transient molecules with from 7 to 16 atoms, as well as for smaller species for which no electronic spectral data are available, will be the subject of a third compilation which is currently being prepared. It is planned to maintain these data files, with continuous upgrading at NIST. Network access to the current file and the conversion of the tables to data base format in order to permit range searches are currently being implemented.

5.0 SENSITIVITY ANALYSIS AS A CRITICAL CROSS-CONNECTION

5.1 Background and Overview of the Role of Sensitivity Analysis

In recent years, the confluence of sophisticated new laboratory and computational tools has led to a more systematic approach to treating complex problems, particularly at the interface of applied and fundamental science. The general problem of understanding energetic materials ignition and combustion for nitramine propellants also falls into this category. As explained in the introduction, sufficient experimental, theoretical and modeling information has been assembled to reach the necessary critical threshold allowing for further accelerated progress, provided a systematic approach is taken.

The successful treatment of problems arising, for example, in atmospheric chemistry and hydrocarbon combustion is largely due to a similar confluence of conceptual, laboratory, and numerical tools. It is the thesis of this paper that a similar effort is now appropriate for the treatment of energetic materials combustion.

Furthermore, we want to emphasize the critical introduction of sensitivity analysis tools into this effort.[149,150] These tools have already begun to have an impact on unravelling the complexities of hydrocarbon combustion,[151] and we propose here a full extension and exploitation of their capabilities for the problem at hand. Indeed, it is clear that progress will be significantly slower without the full integration of sensitivity techniques and concepts to evaluate and guide further research on energetic materials decomposition.

The mathematical concepts underlying sensitivity analysis have a long history, rooted in the work of Poincare's stability analysis. With the rapid development of nuclear energy after the 1940's, sensitivity analysis techniques were seriously pursued to support nuclear engineering reactor design efforts. Applications and development to a lesser degree were also pursued in other areas of engineering as well as economics and other fields. As exemplified in the previous sections of this report, and more elaborately explained below, the iterative process of theoretical studies, modeling and experiment inevitably raise a generic set of issues and questions. This circumstance has allowed the general concepts of sensitivity analysis to be pursued and exploited in a broad sector of applied topics. However, quite surprisingly only in the last several years has serious pursuit of analogous developments and applications in chemistry and physics been seriously considered.[149-151]

It is not our purpose here to comment on this disparity in development, but rather to suggest full exploitation and further development of these capabilities with a particular emphasis on the scientific problems arising in energetic materials decomposition and combustion. As will be described below, this matter involves a dual effort of exploitation of existing sensitivity techniques as well as an identification of the need to develop new theoretical tools to extend the technique capabilities even further. An effort will be made to point out how the sensitivity tools may be beneficially applied to the overall classes of problems encountered in filling out an understanding of the processes illustrated in Figure 2.

5.2 Overall Capabilities of Sensitivity Analysis

The purpose of this subsection is to provide the explicit definitions and underlying interpretation of the variety of sensitivity coefficients needed in energetic materials combustion research. No attempt will be made here to seriously discuss the underlying mathematical or numerical analysis since extensive articles and review papers are available for further details.[149-151]

However, in this regard, we do emphasize the importance of fully considering the specialized numerical needs of sensitivity analysis when developing computational coding for theoretical or modeling efforts. In general, if computational modeling and theoretical studies are feasible, then quite simply their sensitivity analysis is also feasible, and necessary to fully extract the information content of the studies.

The discussion below is in reference to Figure 7, which depicts the overall family of sensitivity techniques relevant to energetic materials combustion. The chemical species or other dependent variables will be denoted as $O_i(x,t)$ which is the i^{th} member of the set, x refers to the coordinate variable(s) and t is time. General parameters arising in the physical problems will be denoted by $\alpha_1, \alpha_2, \alpha_3, \ldots$

5.2.1 Identification of Key Dependent Variables and Chemical Pathways

Even before consideration of critical chemical parameters, there is the more basic need to identify which chemical species or dependent variables are important in macroscopic kinetics as well as the analogous goal of identifying the important degrees of freedom in dynamics phenomena. Taking energetic material kinetics as an example, a simple identification of concentration magnitude or chemical fluxes is always a valuable guide. This information is especially important for determining which small concentration, difficult to measure radicals are important. However, a particular sensitivity test is specifically applicable here.

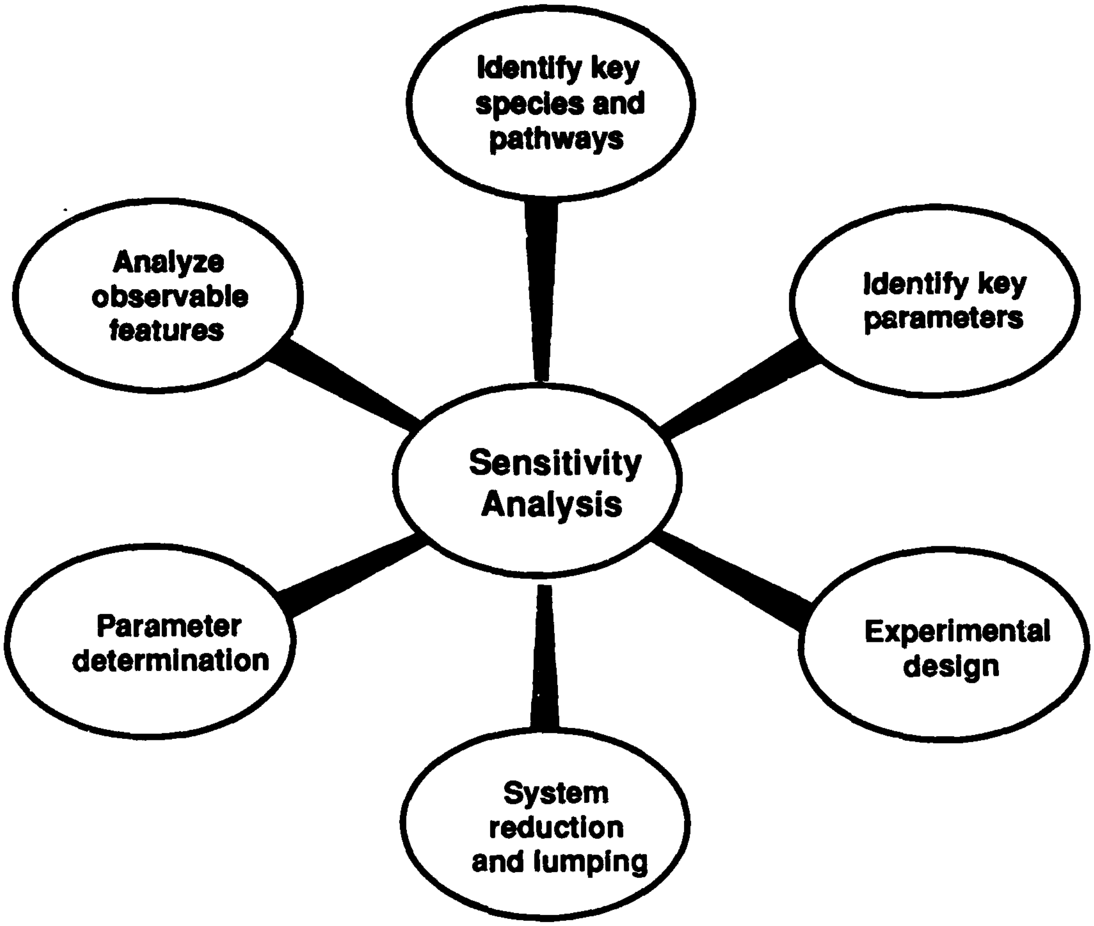

Figure 7. Illustration of the Central Role of Sensitivity Analyses in Coordinated, Hierarchial Theoretical/Experimental Research Programs

One may calculate elements of the so-called Green's function matrix $\delta O_i/\delta J_n$ where δJ_n can be thought of as an incremental flux of the n^{th} dependent variable. Therefore, the elements of the Green's function matrix provide a direct measure of the dynamic interconnectivity between the chemical species. Such an interconnectivity will most frequently go beyond what is reflected in the chemical mechanism alone due to the strong coupling inherent in energetic materials combustion. Furthermore, elements of this matrix are in principle measurable in the laboratory by the introduction of a flux of a particular disturbing species. It is also possible to calculate constrained Green's functions to identify explicitly dynamic pathways for the interconnection of the chemical species. This type of identification may provide key insight for suggested modification of the energetic materials themselves. Issues analogous to these also arise at the dynamics level for the identification of important degrees of freedom or pathways in bimolecular or unimolecular process. Such information could be used to guide the improvement of dynamics calculations of critical kinetic rate constants.

5.2.2 Identification of Key Parameters

Certainly a recurrent theme throughout all levels of the effort as shown in Figure 2 is the desire to identify the important parameters. This goal is for the purpose of ultimate model simplification as well as identification of further theoretical and experimental research to define better the identified critical parameters. The sensitivity coefficients $S_{ij} = \partial O_i/\partial \alpha_j$ provide the direct means to guide these studies. The magnitude and sign of these coefficients signifies the system's response to the parameters being probed. In the case of energetic materials kinetic modelling, the parameters would consist of rate constants, transport coefficients, initial conditions, boundary conditions, etc.[17,18,151]

For molecular dynamics an extension of these concepts into the functional domain is important. This need arises because, for example, a potential surface governing dynamics is a function of the dynamical coordinates even if, in practice, it is parameterized for convenience. Therefore, the basic sensitivity coefficient in this case now has the form:

$$S_i(x) = \delta O_i/\delta V(x).$$

A similar set of functional sensitivity coefficients would also arise when desiring to know which orbital regions at the electronic level actually control the ultimate dynamic and kinetic behavior. In this case, the input functional variation would be with respect to the wavefunction, and we desire to probe how the electronic wave function controls behavior at the higher dynamical or kinetic level.

5.2.3 Analysis of Critical Laboratory Signatures

Laboratory experiments on energetic materials will typically produce temporal and/or spatial profiles of chemical concentrations, temperature, spectral intensities, etc. Each of these observable profiles has its own characteristics, and one can often identify features of special interest including thresholds, peak locations, widths, etc. Variables identifying these features are typically located at particular spatial and/or temporal coordinates. The natural question then arises as to how the observable critical values for these coordinates depend on the underlying system model, structure, or parameters. As an example, one may calculate the sensitivity of the induction time τ for explosion with respect to the underlying system parameters or dependent variables, respectively $\partial\tau/\partial\alpha_i$ and $\delta\tau/\delta O_i$. In essence, these sensitivity gradients provide a direct connection between the parameters meaningful at the theoretical or modeling level and those of special importance at the observable laboratory level.[152] A probing of this type could extend from one extreme of hierarchy in Figure 2 to the other, ultimately addressing the connection between engineering energetic materials behavior and the fundamental driving sources at the electronic level.

5.2.4 Experimental Design

Modeling and theory separately have an important role in this effort, but their full utility will only be achieved when they are interconnected with the laboratory studies. Many of the kinetics, dynamics or spectroscopic measurements planned as part of energetic materials research will be performed to determine one or more critical parameters such as rate constants, radiative lifetimes, spectral constants, etc. The true connection between the measurements and the desired parameters can be obscure in many cases where "clean" experiments cannot be easily devised. However, the desired connection can be provided through the linking concepts of sensitivity analysis. In particular, inverse gradients such as $\partial\alpha_i/\partial O_j$ can provide explicit guidance on whether the performance of the j^{th} measurement O_j is likely to be relevant for identifying the i^{th} system parameter α_i. At an even deeper level, after performance of the j^{th} measurement O_j, one can ask whether any significant information is to be gained by additionally performing the k^{th} measurement O_k. This question may be addressed by further calculating the derived sensitivity $(\partial O_k/\partial O_j)$ where a small value of this derivative will indicate independence of these two measurements and hence the worthiness of performing the k^{th} observation. This point is especially important for energetic material combustion where the complexities of the problem preclude performing all possible or even a modest fraction of the possible measurements.

In a similar vein, parameter correlation coefficients $(\partial\alpha_i/\partial\alpha_j)$ may be calculated where they are implicity understood to correspond to a particular subset of the dependent variables held fixed. In other words, they address the question of whether a correlated response in parameter α_i can be made to compensate for one in parameter α_j and still leave the observations invariant. This question is especially important when attempting to identify whether a decomposition model is unique or if a family of models might suffice to produce the same or similar observations. A point to understand is that these gradients may be calculated independently of the statistical error analysis with experimental data, since they represent correlation inherent in the dynamics or kinetics models.

5.2.5 Critical Parameter Identification of Statistical Error Analysis

Experiments throughout the hierarchy in Figure 2 will be performed to gain insight, identify chemical species or dependent variables of importance and most significantly, to provide parameters as input to refine models. In the latter category, one always desires to perform the cleanest experiment possible to isolate the parameters of interest. However, in practice this may not always be possible especially for the identification of parameters only associated with phenomena (e.g., burning rate) in the bulk energetic material. In this latter case, it is only possible reliably to extract the parameters by simultaneously performing a modeling and sensitivity analysis and combining them with the available data. With such a treatment one must consider errors arising in the experimental data, the form of the model and its "known" other parameters. In thermal decomposition problems, form refers to the proposed mechanism and the "known" parameters refers to those specified from other experiments. The sensitivities referred to in Subsection 5.2.4 are especially important in executing this analysis. The ultimate goal is to achieve a quantitative measure of uncertainty in the extracted parameters. One cautionary comment is that sensitivity analysis exploited in this way is in general restricted to the regime of a local analysis due to its first order gradient nature. Partially in recognition of this point, Subsection 5.3.1 below makes specific suggestions for accordingly extending the sensitivity analysis tools.

5.2.6 Lumped Model Identification

It was argued in Section 3.6 that there is an essential need to reduce the complexities of the microscopic dynamic and macroscopic kinetic models to their physical essence as much as possible. Sensitivity analysis is not the only tool to be exploited for this purpose, but it can have a significant role. At a minimum, its contribution can consist of providing a quantitative indicator of the viability of system lumping and reduction. In particular, the phenomena of scaling and self similarity among the sensitivity coefficients of various types, implies a distinct underlying dynamically driven relationship among either the system dependent variables or the parameters themselves.[150,153]

Furthermore, it may be possible directly to estimate the combination(s) of dependent variables or parameters appropriate for the reduced or lumped systems. The presence of scaling and self similarity is proving to be one of the more important generic results to arise from sensitivity analysis and a full exploration of its consequences should be a natural part of planned research in this area.

The above narrative list of energetic materials applications of sensitivity analysis as depicted in Figure 7 will likely grow and be amended as the tools are further developed and implemented. This latter comment is based on experience with parallel sensitivity analysis pursuits in other physical areas of application.

5.3 Specific Research Needs for Advancing Energetic Materials Relevant To Sensitivity Analysis Techniques

Sensitivity analysis is beginning to make a contribution to energetic materials combustion,[17,18,154] and a further step is surely a complete implementation of the currently available techniques. However, clear needs can already be identified for improving these techniques in order for the fullest understanding of energetic materials decomposition to be made as rapidly as possible. Two specific suggestions for pursuit are listed below.

5.3.1 Extension of Sensitivity Gradient Concepts to the Electronic Structure Level

Although this extension does not directly represent a fundamental alteration in the existing tools, it does represent an extension to the most fundamental level. This extension would finally complete the hierarchy of bridging steps that sensitivity analysis can provide, ranging from the electronic structure level through macroscopic processes. It is important to understand that the issues here are not ones questioning structure in the electronic Hamiltonian, but rather the role played by that structure and, perhaps more important, the contributions of different orbitals for steering reactive processes into one channel or another. Sensitivity analysis has the potential for providing a quantitative assessment of these matters beyond the loose qualitative discussion of their treatment in the existing literature. Another related matter would be the use of sensitivity analysis to identify the most important locations for sampling potential surfaces used in subsequent dynamics for rate constant estimation. Naturally, all these applications are themselves associated with iterative processes of improvement at the electronic level as guided through the sensitivity of rates or even higher level observables to the underlying microscale processes.

5.3.2 Global Sensitivity Analysis

All of the sensitivity concepts discussed throughout this paper are based on local gradient sensitivity analysis techniques. The local concepts are especially useful for addressing the question of what's important in a nominal energetic material or in a model of one that is undergoing iterative improvement. On a broader scale is the desire to feed this information ultimately into the design process of providing improved propellant molecules or mixtures. Here, sensitivity on a more global scale with respect to controlling parameters is critical. A successful treatment of this matter would have widespread applications to many topics besides the one being treated here. However, a global assessment of any problem will never be an inexpensive matter, although it need not be as costly as the brute force approach of repeated computational sampling in parameter space. Currently, research in the area of using Lie groups for this goal is being pursued and this activity should be explored carefully and other approaches encouraged as well.[79]

The entire effort being proposed here, including that of development and application of sensitivity analysis, represents an overall generic approach to the treatment of complex problems. It is worthy to note that full pursuit of this research for the immediate energetic materials applications would also lay the direct groundwork for the transferral of the methodology to analogous complex problems in science and engineering.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The effective and efficient development of new generations of nitramine based, highly energetic propellants clearly will require the systematic acquisition, integration and exploitation of a much deeper knowledge of the basic physics and chemistry controlling the ignition and combustion of both neat nitramines and nitramine based propellant formulations.

The acquisition of the needed depth of understanding will require a coordinated hierarchical program involving both extensive theoretical modeling and supporting and confirming experimental work as outlined in Figure 2.

The components of the required basic research program discussed in depth in Sections 3 through 5 of this report are summarized below. All of the specific components of the required research plan cannot be presented at this time, principally because of the interactive nature of the program represented by Figure 2. New issues will be uncovered and highlighted as the research progresses. As discussed in Sections 2 and 4 one key question, yet to be answered, is how important condensed phase and gas-surface physical and chemical processes are in controlling the ignition mechanism and burning rate.

While all of the details of a successful nitramine based propellant ignition and combustion research program can not yet be set, we firmly believe that the major components are clear and that no technical barriers exist to prevent the implementation of a successful and productive research initiative aimed at placing highly energetic nitramine propellant development activities on a firm scientific basis.

6.2 Recommendations

6.2.1 Technical Issues

A research program focused on understanding and integrating the basic physical and chemical processes controlling the ignition and combustion of nitramine propellants should be initiated as soon as possible.

The basic goal of such a program should be to generate a set of comprehensive computer models capable of describing the pyrolysis and subsequent combustion of a wide variety of known and prospective nitramine compounds, both alone and formulated with a wide range of binders and other propellant components.

These models must be validated against a comprehensive set of careful experimental measurements from a variety of pyrolysis and combustion experiments on both nitramine propellant components and formulations. The quality of this validating experimental data will depend heavily on the creative adaptation and/or invention of precise diagnostics for critical physical properties and key chemical species distributions.

Model development efforts must be systematic, with steady progression from the simpler to the more complex, and with constant experimental validation as outlined in Table 1 of Section 3.

Critical thermochemical, kinetic and heat, mass, and radiative transfer parameters will have to be generated for a variety of nitramine species and their decomposition and reaction products. Key spectral and radiative parameters will also be required for diagnostic development and tailoring. The successful generation of these required microphysical "input" parameters will require a large number of supporting theoretical and experimental studies, as discussed in Sections 3 and 4.

Sensitivity analysis techniques will be required to guide both theoretical model development and the continuous interplay between models and experiments. As outlined in Section 5, we also believe it has a key role to play in both detailed experimental design and model development. Significant opportunity now exists to extend the capability of sensitivity analysis techniques within the proposed program; these should be pursued.

Finally, the complex models developed for detailed comparison with experiment must be successfully "collapsed" into forms suitable for development engineering. The key to successful model reduction lies in developing procedures and criteria to lump related chemical kinetic and physical transformation processes. Since our final goal is to generate both tractable and accurate engineering development models of nitramine ignition and combustion, it is clear that a significant effort must be devoted to this effort.

6.2.2 Programmatic Issues

A successful program of the type envisioned in this report proceeds through an iterative cycle of:

Problem Definition → Tool Development → Tool Deployment →
→ Problem Solving → Problem Redefinition.

Such a cycle requires time, typically four to six years for each cycle. After the first cycle important engineering tools will be available for the propellant development community; however, at least two cycles will be required to answer all of the most critical needs of that community.

To be successful the proposed program must also be focused. It must be prepared to draw on the best scientists and facilities from university, private and government laboratories. Furthermore, these scientists must have a sense of community to achieve the necessary level of interplay and feedback between various theoretical and experimental efforts.

The creation of this sense of community will require very close cooperation among the program managers funding the effort. It is important that the program have sufficient scientific guidance to insure close cooperation without stifling individual scientific initiative. This balance should be assured by the creation of a scientific advisory panel to help set criteria for proposal submission and review, call and moderate regular technical exchange meetings and counsel program managers on the evolution of programmatic needs and goals.

Furthermore, such an advisory group could be charged with creating and maintaining an effective and dynamic interface with the advanced propellant development and engineering community. Such an interface is critical to the successful transfer of the knowledge gained by the program into engineering reality.

Finally, a hierarchical basic research program as depicted in Figure 2 is not possible without a critical mass of scientific and engineering talent. To make serious progress on the difficult problem of adequately understanding nitramine ignition and combustion will require a substantial effort, and therefore substantial funding.

We estimate that six to ten active research groups will be required for model development and supporting theoretical work during the first four to six year program cycle. Similarly six to ten experimental groups will be needed for smaller scale supporting laboratory experiments and diagnostic development efforts. Finally, two to four major laboratory facilities must be involved in larger scale propellant and propellant component pyrolysis, ignition and burning experiments in order to generate the data necessary to validate both the more complex scientific models and their "reduced" engineering versions.

While the challenge and expense of the nitramine ignition and combustion research program we have outlined may seem formidable, we are convinced it is small compared to the challenge and expense of successfully developing highly energetic nitramine based propellants without it.

7. ACKNOWLEDGMENTS

The study group gratefully acknowledges the intellectual inspiration and encouragement of R.W. Shaw, as well as the financial support of its sponsor, the Chemical and Biological Sciences Division of the U.S. Army Research Office.

We also wish to thank K.K. Kuo of Pennsylvania State University, R.A. Yetter of Princeton University, and R.A. Fifer and G.F. Adams of the U.S. Army Ballistics Research Laboratory for their technical input and insight.

Finally, we thank our hosts, the faculty and staff of the University of North Carolina at Chapel Hill, in general, and T. Baer and R.E. Miller, in particular, for their warm hospitality and support.

8. REFERENCES

1. Boggs, T.L., "The Thermal Behavior or Cyclotrimethylene - trinitramine (RDX) and Cyclotetramethylene tetranitramine (HMX)," in "Fundamentals of Solid-Propellant Combustion", K.K. Kuo and M. Summerfield, Eds., Prog. in Aeronautics and Astronautics 90, 121 (1984)

2. Fifer, R.A., "Chemistry of Nitrate Ester and Nitramine Propellants," in "Fundamentals of Solid-Propellant Combustion", K.K. Kuo and M. Summerfield, Eds., Prog. in Aeronautics and Asatronautics 90, 177 (1984)

3. Schroeder, M.A., "Critical Analysis of Nitramine Decomposition Data: Activation Energies and Frequency Factors for HMX and RDX Decomposition," Report No. BRL-TR-2673, Ballistics Research Laboratory, Aberdeen Proving Ground, MD (September 1985); Schroeder, M.A., "Critical Analysis of Nitramine Decomposition Data: Product Distributions from HMX and RDX Decomposition," Report No. BRL-TR-2659 (June 1985)

4. Cook, M.D., J. Energ. Materials 5, 257 (1987)

5. Suryanarayana, B., Graybush, R., Autera, J.R., Chem. and Ind. 2177 (1967)

6. Dubovitskii, F.I. and B.L. Korsunski, Russian Chem. Rev. 50, 958-978 (1980) [Uspeki Khimii 50, 1828-1871 (1981)]

7. Shaw, R.W., Jr. and Adams, G.F., Eds., "Diagnostics for Propellant Ignition," Army Research Office (June 1985), DTIC No. B093719.

8. Shaw, R.W., Jr., Johnston, S.C., and Adams, G.F., Eds., "Combustion Probes for Solid Nitramines," Army Research Office (June 1986), DTIC No. A174570.

9. "Atmospheric Ozone 1985," World Meteorological Organization Global Ozone Research and Monitoring Project, V. 1-3, Report No. 16, World Meteorological Organization, Geneva, Switzerland (1985)

10. Watson, R.T., M.J. Prather, and M.J. Kurylo, "Present State of Knowledge of the Upper Atmospheric 1988: An Assessment Report," NASA Ref. Pub. 1208 (August 1988)

11. "Handbook of Chemical Lasers," Gross, R.W.F. and Bott, J.E., Ed. John Wiley and Sons, New York (1976)

12. Stough, J.J.T. and Kerber, R.L., Appl. Optics 14, 2960-2970 (1975)

13. Moffatt, N.K. and Jensen, K.F., J. Electrochem. Soc. 135, 459-470 (1988)

14. Kushner, M.J., J. Appl. Phys. 63, 2532-2550 (1988)

15. Westbrook, C.K. and Dryer, F.L., Prog. Energy Combust. Sci. 10, 1-57 (1984)

16. Basevich, V. Ya, Prog. Energy Combust. Sci. 13, 199-248 (1987)

17. Melius, C.F., "Theoretical Studies of the Chemical Reactions Involved in the Ignition of Nitramines," Presented at the 24th JANNAF Combustion Meeting, Monterey, CA (1987)

18. Melius, C.F., "The Gas Phase Flame Chemistry of Nitramine Combustion," (1988)

19. Hatch, R., 24th JANNAF Combustion Meeting, 1987 Monterey, "Chemical Kinetics Modeling of HMX Combustion," Presented at the 24th JANNAF Combustion Meeting, Monterey, CA (1987)

20. (a) Melius, C. and Binkley, S., Proc. 21st Symposium on Combustion (International), 1953-1963 (1986) and (b) Melius, C. and Binkley, S., 23rd JANNAF Combustion Meeting, Vol. I, 241, Hampton, Virginia (1986)

21. Zhao, X., Hintsa, E.J., and Lee, Y.T., J. Chem. Phys. 88, 801-810 (1988)

22. Lloyd, S.A., Umstead, M.E., and Lin, M.C., J. Energ. Materials, in press (1988)

23. Flournoy, J.M., J. Chem. Phys. 36, 1106 (1962)

24. Robertson, A.J.P., Trans. Faraday Society 36, 1106 (1949)

24a. McMillen, D.F., Nigenda, S.E., Gonzalez, A.C., and Golden, D.M., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.) Army Research Office, 14-33 (1986), DTIC No. A174570.

25. Tsang, W. and Hampson, R.F., J. Phys. Chem. Ref. Data, 15, 1087 (1986) and subsequent publications in this series.

26. Johnston, H.S., "Gas Phase Reaction Rate Theory," Ronald Press, New York (1966)

27. Robinson, P.J. and Holbrook, K.A., "Unimolecular Reactions," Wiley-Interscience, New York (1972)

28. Crosley, D.R., Opt. Eng. 20, 511-521 (1981); Crosley, D.R. and Smith G.P., Combust. Flame 44, 27-41 (1982)

29. Anderson, W.R., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.) Army Research Office, 155-161 (1986), DTIC No. A174570.

30. Adams, G.F. and Lengsfield, B.H., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.) Army Research Office, 220-223 (1986), DTIC No. A174570.

31. "Advanced Theories and Computational Approaches to the Electronic Structure of Molecules," C.E. Dykstra, ed., D. Reidel, Amsterdam (1984)

32. Dalgaard, E. and Jorgensen, P., J. Chem. Phys. 69, 3833 (1978)

33. Bauschilcher, C.W. and Yarkony, D.R., J. Chem. Phys. 72, 1138-1144 (1980)

34. Shephard R. and Simons, J., Int. J. Quantum Chem. Symp. 14, 211 (1980); R. Shephard, I.

Shavitt and J. Simons, J. Chem. Phys. 76, 543-557 (1982)

35. Werner, H.-J. and Meyer, W., J. Chem. Phys 74, 5794-5801 (1981)

36. Werner, H.-J. and Knowles, P.J., J. Chem. Phys. 82, 5053-5063 (1985); Knowles, P.J. and Werner, H.-J., Chem. Phys. Lett. 115, 259-267 (1985)

37. Lengsfield, B.H., J. Chem. Phys. 73, 382-389; Lengsfield, B.H. and Liu, B., ibid. 75, 478-480 (1981)

38. Diffenderfer, R.N. and Yarkony, D.R., J. Phys. Chem. 86, 5098-5105 (1982)
39. Saxon, R. and Yoshimine, M., to be published

40. Mowrey, R. and Page, M., to be published

41. Herzberg, G., "Molecular Spectra and Molecular Structure. I. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand Reinhold, New York (1966)

42. Alexander, M.H., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.) Army Research Office, 255-257 (1986), DTIC No. A174570.

43. See, for example, Colton, M.C. and Schatz, G.C., J. Chem. Phys. 83, 3413-3425 (1985)

44. Gally, G. and Lorquet, J.-C., J. Chem. Phys. 67, 4672-4680 (1977); Desouter-Lecomte, M., Gally, G., Lorquet, J.-C. and vaz Pires, M., ibid. 71, 3661-3672 (1979)

45. Hirsch, G., Bruna, P.J., Buenker, R.J., and Peyerimhoff, S.D., Chem. Phys. 45, 335-347 (1980); Buenker, R.J., Hirsch, G., Peyerimhoff, S.D., Bruna, P.J., R`melt, J., Bettendorf, M., and Petronogolo, C., "Current Aspects of Quantum Chemistry 1981," R. Carbo, Ed., Elsevier, Amsterdam (1982)

46. Lengsfield, B.H., Saxe, P., and Yarkony, D.R., ibid. 81, 4549-4553 (1984); Lengsfield, B.H., and Yarkony, D.R., ibid. 84, 348-353 (1986); Yarkony, D.R., J. Chem. Phys. 84, 3206-3211 (1986); Saxe, P. and Yarkony, D.R., ibid 86, 321-328 (1987)

47. Werner, H.-J., Follmeg, B., and Alexander, M.H., J. Chem. Phys., 29, 3139-3151 (1988).

48. Nikitin, E.E., J. Chem. Phys. 43, 744-750 (1965); Nikitin, E.E., Adv. Chem. Phys. 28, 317-377 (1975); Nikitin, E.E. and Umanskii, S. Ya., "Theory of Slow Atomic Collisions," Springer-Verlag, Berlin (1984)

49. Reid, R.H.G., J. Phys. B 6, 2018-2039 (1973)

50. Mies, F.H., Phys. Rev. A 7, 942-957 (1973)

51. Masnou-Seeuws, R. and MacCarroll, R., J. Phys. B 7, 2230-2243 (1974)

52. Voronin, A.L. and Kvilividze, V.A., Theor. Chim. Acta. 8, 334-340 (1967)

53. Preston, R.K., Sloane, S., and Miller, W.H., J. Chem. Phys. 60, 4961-4969 (1974)

54. Aquilanti, V. and Grossi, G., J. Chem. Phys. 73, 1165-1172 (1980); Aquilanti, V.,

Casavecchia, P., Grossi, G., and Lagana, A., ibid. 73, 1173-1180 (1980); Aquilanti, V., Grossi, G., and Lagana, A., Nuovo Cimento 63B, 7-14 (1981)

55. Alexander, M.H., Orikowski, T., and Straub, J.E., Phys. Rev. A28, 73-82 (1983); Pouilly, B., Orlikowski, T. and Alexander, M.H., J. Phys. B18, 1953-1967 (1985); D. Lemoine, J.-M. Robbe, and Pouilly, B., J. Phys. B.21, 1007-1025 (1988)

56. Alexander, M.H. and Pouilly, B., in "Selectivity in Chemical Reactions," (J.C. Whitehead, Ed.), 265-306 (Kluwer Academic, Dordrecht, 1988).

57. Pouilly, B. and Alexander, M.H., J. Chem. Phys. 86, 4790-4800 (1987)

58. Hertel, I.V., Schmidt, H., Bahring, A., and Meyer, E., Rep. Prog. Phys. 48, 375 (1985); Reiland, W., Jamieson, G., Titles, U., and Hertel, I.V., Z. Phys. A.307, 51-66 (1982)

59. Hess, B.A., Buenker, R.J., Marian, C.M., and Peyerimhoff, S.D., Chem. Phys. 71, 79-85 (1982); Chem. Phys. Lett. 89, 459-462 (1982)

60. Havriliak, S.J. and Yarkony, D.R., J. Chem. Phys. 83, 1168-1172 (1985); Jensen, J.O. and Yarkony, D.R., Chem. Phys. Lett. 141, 391-396 (1987)

61. Langhoff, S.R., Bauschlicher, C.W., and Partridge, H., Intern. J. Quantum Chem. Symp. 18, 457-466 (1985)

62. Benyon, J.H. and Gilber, J.R., "Application of Transition State Theory to Unimolecular Reactions," Wiley, New York (1984)

63. Pritchard, H.O., "The Quantum Theory of Unimolecular Reactions," Cambridge University Press, Cambridge, U.K. (1984)

64. Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B., Molecular Theory of Gases and Liquids, Wiley, New York (1954)

65. McDaniel, E.W. and Mason, E.A., "The Mobility and Diffusion of Ions in Gases," Wiley, New York (1973)

66. Alexander, M.H., J. Chem. Phys. 81, 4510-4516 (1984); Alexander, M.H. and Manolopoulos, D.E., ibid. 86, 2044-2050 (1987)

67. Benson, S.W., "Thermochemical Kinetics," John Wiley, New York (1976)

68. Chase, M.W. Jr., Davies, C.A., Downey, J.R. Jr., Grurip, D.J., McDonald, R.A., and Syverund, A.N., JANNAF Thermochemical Tables, Third edition, J. Phys. Chem. Ref. Data 14, Supplement No. 1 (1985)

69. Pedley, J.B., Naylor, R.D., and Kirby, S.P., "Thermochemical Data of Organic Compounds," 2nd edition, Chapman and Hall, London (1986)

70. Young, J.A., Keith, J.E., Stehle, P., Dzomback, W.C., and Hunt, H., Ind. Eng. Chem. 48, 1375 (1956)

71. Culick, F.E.C., AIAA Journal 6, 2241 (1968)

72. Beckstead, M.W., Derr, R.L., and Price, C.F., AIAA Journal 8, 2200 (1970)

73 Levy, A. and Weinberg, F.J., *Seventh Symposium (International) on Combustion*, Pittsburgh, 296 (1959)

74. Levy, A. and Weinberg, F.J., Comb. and Flame 3, 229 (1959)

75. Westbrook, C.K. and Dryer, F.L., Comb. Sci. and Tech. 27, 31 (1981)

76. Coffee, T.P., Kotlar, A.J., and Miller, M.S., Comb. and Flame 54, 155 (1983)

77. Kuo, J. and Wei, J., Ind. Eng. Chem. Fund. 8, 114 (1969)

78. Li. G., Chem. Eng. Sci. 39, 1261 (1984)

79. Wulfman, C. and Rabitz, H., J. Phys. Chem. 90, 2264-2272 (1986)

80. Kubota, N., in Fundamentals of Solid Propellant Combustion (Kuo, K. and Summerfield, M., Eds.), Progress in Astronautics and Aeronautics 90, 1-52 (1984)

81. Bulusu, S., Weinstein, D.I., Autera, J.R., and Velicky, R.W., J. Phys. Chem. 90, 4121-4126 (1986)

82. Shackelford, F.A., et al. J. de Physique 48, Colloq. C4, 193-207 (1987)

83. Korobeinichev, O.P., et al., in Mass Spectrometry and Chemical Kinetics, Moscow, 73-93; Ermolin, N.E., Korobeinichev, O.P., Kuibida, L.V., and Fomin, V.M., Fiz. Goreniya Vzryva 22, 54-64 (1986)

84. Kubota, N., Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 777-785 (1982)

85. Druet, S.A.J. and Taran, J.P.E., Progress in Quantum Electronics, 7, 1-72 (1981)

86. Hall, R.J. and Eckbreth, A.C., in "Laser Applications 5," (Ready, J.F. and Erf, R.K., Eds.), 213-309 (Academic Press, New York) (1984)

87. Eckbreth, A.C., Dobbs, G.M., Stufflebeam, J.H., and Tellex, P.A., Appl. Optics 23, 1328-1339 (1984)

88. Stufflebeam, J.H. and Eckbreth, A.C., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.), Army Research Office, 188-211 (1986)

89. Murphy, D.V., Long, M.B., Chang, R.K., and Eckbreth, A.C., Optics Letters 4, 167-169 (1979)

90. Heller, C.A. and Gordon, A.S., J. Phys. Chem. 59, 773-777 (1955)

91. Snyder, P.A., Kremer, J.H., Liebmann, S.A., Schroeder, M.A., and Fifer, R.A., Organic Mass Spectrometry, in press

92. Behrens, R., in Combustion Probes for Solid Nitramines (Shaw, R.W., Johnston, S.C., and Adams, G.F., Eds.) Army Research Office, 50-82 (1986), DTIC No. A174570.

93. Mal'tsev, V.M., Stasenko, A.G., Selezner, V.A., and Pokhil, P.F., Fiz. Goreniya Vzryva 9, 220-225 (1973)

94. Edwards, T., Weaver, D.P., Campbell, D.H., and Hulsizer, S., J. Propulsion Power 2, 228-236 (1986)

95. Renlund, A.M. and Trott, W.M., J. de Physique 48, Colloq. C4, 179-188 (1987)

96. Fontijin, A., Ed. "Gas-Phase Chemiluminescence and Chemi-Ionization," North-Holland, Amsterdam (1985)

97. Gorbal, M.R. and Savadatti, M.I., Chem. Rev. 82, 527-540 (1982)

98. Solomon, P.R., Best, P.F., Carangelo, R.M., Markham, J.R., Chien, P.-L., Santoro, R.J., and Semerjian, H.G., Twenty-First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1763-1771 (1986)

99. Pfeil, A., Eisenreich, N., and Krause, H., J. de Physique 48, Colloq. C4, 209-221 (1987)

100. Bent, H.A. and Crawford, B. Jr., J. Phys. Chem. 63, 941-952 (1959)

101. Karpowicz, R.J. and Brill, T.B., J. Phys. Chem. 88, 348-352 (1984)

102. Brill, T.B. and Oyumi, Y., J. Phys. Chem. 90, 2679-2682 (1986)

103. Edwards, T., Proceedings of the 24th JANNAF Combustion Meeting, CPIA Publication 476, 1, 235-242 (1987)

104. Parr, T. and Hanson-Parr, D., Proceedings of the 24th JANNAR Combustion Meeting, CPIA Publication 476, 1, 367-382 (1987)

105. Crosley, D.R., Ed., "Laser Probes for Combustion Chemistry," Amer. Chem. Soc. Symposium Series 134 (1980)

106. Crosley, D.R. and Smith, G.P., Opt. Eng. 22, 545-553 (1983)

107. Bechtel, J.H., Dasch, C.J., and Teets, R., in "Laser Applications 5" (Ready, J.F. and Erf, R.K., Eds.), 129-212 Academic Press, New York (1983)

108. Lucht, R.P., in "Laser Spectroscopy and Its Applications," Radziemski, L.J., Solarz, R.W., and Paisner, J.A., Eds., Marcell Dekker, New York, 623-376 (1986)

109. Garland, N. and Crosley, D.R., Twenty-First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1693-1702 (1986)

110. Daily, J.W., Appl. Opt. 15, 955-960 (1976)

111. Lucht, R.P., Sweeney, D.W., Laurendeau, N.M., Drake, M.C., Lapp. M., and Pitz, R.W., Opt. Lett 9, 90-92 (1984)

112. Kohse-Hoinghaus, K., Heidenreich, R., and Just, Th., Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1177-1185 (1985)

113. Hanson, R.K., Twenty-First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1677-1691 (1986)

114. Jeffries, J.B., Copeland, R.A., Smith, G.P., and Crosley, D.R., Twenty-First Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1709-1718 (1986)

115. Goldsmith, J.E.M., Opt. Lett. 7, 437-439 (1982); Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1331-1337 (1985); Appl. Opt. 26, 3566-3572 (1987)

116. Bamford, D.J., Jusinski, L.E., and Bischel, W.K., Phys. Rev. A34, 185-198 (1986)

117. DiGiuseppe,T.G., Hudgens, J.W., and Lin, M.C., J. Phys. Chem. 86, 6-41 (1982)

118. Tjossem, P.J.H., Goodwin, P.M., and Cool, T.A., J. Chem. Phys. 84, 5334-5343 (1986)

119. Bischel, W.K., Perry, B.E., and Crosley, D.R., Appl. Opt. 21, 1419-1429 (1982)

120. Alden, M. Hertz, H.M., Svanberg, S., and Wallin, S., Appl. Opt. 23, 3255-3257 (1984)

121. Goldsmith, J.E.M. and Anderson, R.J.M., Appl. Opt. 24, 607-609 (1985)

122. Bittner, J., Kohse-Hoinghaus, K., Meier, U., Kelm, S., and Just, Th., Combust. Flame 71, 41-50 (1988)

123. Dagdigian, P.J., Forch, B.E., and Miziolek, A.W., Chem. Phys. Lett., 148, 299-308 (1988).

124. Dalby, F.W., Can. J. Phys. 36, 1336-1371 (1958)

125. Dixon, R.N., Phil. Trans. Roy. Soc. (London) A252, 165-169 (1960)

126. Oglivie, J.F. and Horne, D.G., J. Chem. Phys. 48, 2248-2256 (1968); Horne, D.G. and Norrish, R.G.W., Proc. Roy. Soc. (London) A315, 301-315 (1970); Ogilvie, J.F., Can. J. Spectrosc. 19, 89-95 (1974)

127. Jacox, M.E., J. Molec. Spectrosc. 113, 286-301 (1985)

128. Jacox, M.E., J. Molec. Struct. 157, 43-59 (1987)

129. Jacox, M.E., J. Phys. Chem. 91, 6595-6600 (1987)

130. Jacox, M.E. and Olson, W.B., J. Chem. Phys. 86, 3134-3142 (1987)

131. Duxbury, G., Kato, H., and LeLerre, M.L., Faraday Discuss. Chem. Soc. 71, 97-110 (1981); Duxbury, G. and LeLerre, M.L., J. Molec. Spectrosc. 92, 326 -348 (1982); Hamada, Y., Hashiguchi, K., Tsuboi, M., Koga, Y., and Kando, S., J. Molec. Spectros. 105, 70-80 (1984)

132. Balla, R.J. and Pasternack, L., J. Phys. Chem. 91, 73-78 (1987)

133. Kanamori, H., Butler, J.E., Kawaguchi, K., Yamada, C., and Hirota, E., J. Chem. Phys. 83, 611-615 (1985)

134. Radhakrishnan, G., Parr, T., and Wittig, C., Chem. Phys. Lett. 111, 25-32 (1984)

135. Beyer, R.A. and Morgan, C.U., Proceedings of the 16th JANNAF Combustion Meeting, CPIA Pub. 308, II, pp. 51-57 (1979); Morgan, C.U. and Beyer, R.A., Combust. Flame 36, 99-101 (1979)

136. Hudgens, J.W., "Advances in Mutli-photon Processes and Spectros. 4", S.H. Lin, Ed., World Scientific Publishing Co., Singapore, 171-296 (1988)

137. Tsang, W., in "Shock Waves in Chemistry" Lifshitz, A., Ed., Marcel Dekker, New York, 60 (1981)

138. Howard, C.J., J. Phys. Chem. 83, 3-9 (1979)

139. Liu, A., Mulac, W.A., and Jonah, C.D., J. Phys. Chem. 92, 3828 - 3833 (1988)

140. Tully, F.P., Chem. Phys. Lett. 96, 148-153 (1983)

141. Kaufman, F., Ninteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1-10 (1982)

142. Kaufman, F., J. Phys. Chem. 88, 4909-4917 (1984)

143. Silver, J.A. and Kolb, C.E., J. Phys. Chem. 91, 3713-3714 (1987)

144. Gersh, M.E., Silver, J.A., Zahniser, M.S., Kolb, C.E. Brown, R.G., Gozewski, C.M., Kallelis, S. and Wormhoudt J., Rev. Sci. Instr. 52, 1213-1222 (1981)

145. Huber, K.P. and Herzberg, G., "Molecular Spectra and Molecular Structure. IV. Energy Levels of Diatomic Molecules," Van Nostrand, Princeton, NJ (1979)

146. Herzberg, G., "Molecular Spectra and Molecular Structure. II. "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, NJ (1945)

147. Jacox, M.E., J. Phys. Chem. Ref. Data 13, 945-1068 (1984)

148. Jacox, M.E., J. Phys. Chem. Ref. Data 17, 269-511 (1988)

149. Rabitz, H., Kramer, M., and Dacol, D., Ann. Rev. Phys. Chem. 34, 419 (1983)

150. Rabitz, H. Chem. Revs. 87, 101 (1987)

151. Rabitz, H., in "The Mathematics of Combustion," Buckmaster, J., Ed. (SIAM, Philadelphia) (1985)

152. Skumanich, M. and Rabitz, H., J. Mol. Sci. 2, 79 (1982)

153. Rabitz, H. and Smooke, H., J. Phys. Chem. 92, 1110-1119 (1988)

154. Yetter, R. and Rabitz, H., "Decomposition Kinetics of Propellants: Modelling and Sensitivity Analysis of Homogeneous, Gas-Phase, Nitromethane Decomposition," work in progress