NBS SPECIAL PUBLICATION 531

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Summary Report on the Workshop on High Temperature Chemical Kinetics: Applications to Combustion Research

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Summary Report on the Workshop on High Temperature Chemical Kinetics: Applications to Combustion Research

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M. J. Kurylo, and W. Tsang

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Sponsored by

Department of Energy
Washington, D.C. 20545 and

Office of Standard Reference Data
National Bureau of Standards
Washington, D.C. 20234

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Issued December 1978

Library of Congress Catalog Card Number 78-600125

National Bureau of Standards Special Publication 531
Nat. Bur. Stand. (U.S.), Spec. Publ. 531, 89 pages (Dec. 1978)
CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1978

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Stock No. 003-003-02005-0 Price $2.75
(Add 25 percent additional for other than U.S. mailing).

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D. Garvin, R.L. Brown, R.F. Hampson, M.J. Kurylo, and W. Tsang

Abstract

The proceedings at a workshop on the applications of high temperature chemical kinetics to combustion research are summarized. This workshop, held Dec. 12-13, 1977 at the National Bureau of Standards, provided a forum for the exchange of views on the needs for kinetics research during the next five to ten years. Experimental techniques, measurements, theoretical developments and data evaluation were treated in four review papers and two discussion sessions.

This report contains the program of the meeting, abstracts of the review papers, a commentary by the organizers of the meeting, summaries of the discussions, formal comments submitted by the participants and an attendance list.

Keywords: chemical kinetics, combustion, high temperature chemistry, reaction rate constants, measurement techniques, assessment of needs.

1. Introduction

On December 12 and 13, 1977, a workshop was held at the National Bureau of Standards, Gaithersburg, MD on "High Temperature Chemical Kinetics: Applications to Combustion Research". This workshop was sponsored by the Division of Basic Energy Sciences, Department of Energy and the Office of Standard Reference Data, NBS. It was attended by one hundred persons, mainly chemical kineticists interested in combustion, but also including researchers concerned with the modeling of practical combustion systems and the development of diagnostic techniques for probing such systems.

The objective of the workshop was to provide a forum for an exchange of views on the needs for high temperature chemical kinetics research during the next five to ten years, research that would support the development of improved chemical theoretical developments, experimental measurements and data evaluation.

Speakers and discussion leaders were instructed to attempt to answer the following questions for each topic discussed:

Why it is important in combustion research?
What is the current state of our knowledge?
What do we need to know, and how accurately?
What speculative areas should be explored?
What do you see as the research priorities?

Four invited review papers provided orientation for the participants. These papers covered topics in modeling of combustion, the application of laser diagnostic techniques, combustion chemistry and mechanisms, and the availability of high temperature rate data. Two extensive discussion periods were directed toward needs for high temperature kinetics research and the acquisition of high temperature kinetics data.

This report contains the program of the meeting, abstracts of the invited papers, summaries of the general discussions, written contributions submitted by the participants and a commentary by the organizers of the meeting. An attendance list is appended.

The association of chemical kinetics and combustion is not new. Almost from the start the programs of the International Symposia on Combustion, organized by the Combustion Institute, have featured kinetic studies of individual reactions and of oxidation systems. The journal "Combustion and Flame" regularly features articles on kinetics.

Nor are discussions on the interrelationship of kinetics and combustion research novel, although they have grown in importance recently. In 1974 the National Science Foundation sponsored a "Workshop on Energy-related Basic Combustion Studies" (Glassman and Sirirnano, 1974) that included an analysis of combustion related kinetics. Problems discussed then are still with us today. In September 1977, Project Squid held a "Workshop on: Alternate Hydrocarbon Fuels for Engines: Combustion and Chemical Kinetics" at Columbia, Maryland. It was sponsored jointly by the Department of Energy and the Department of Defense. The kinetics topics covered at that meeting and at the present one overlap extensively. The workshop reported on here has been followed by a "Workshop on Modeling of Combustion in Practical Systems", held at Los Angeles in January 1978, also sponsored by the Department of Energy.

These interdisciplinary meetings indicate a high level of concern for the solution of combustion problems on the part of the sponsors. They have enhanced the knowledge of the participants by exposing them to the problems and needs of workers in disciplines other than their own. Problems requiring early solution become apparent. Continued cross-discipline communication should improve our understanding of the complex phenomenon of chemical combustion.

2. Program of the Meeting

Monday, December 12, 1977

9:15	Welcome and Introductory Remarks E. Horowitz, Deputy Director Institute for Materials Research, NBS J. S. Kane, Director Division of Basic Energy Sciences, DOE
9:30	INVITED PAPERS Session Chairman: L. H. Gevantman, NBS Recent developments in computer modelling of chemical combustion systems. J. S. Chang and C. K. Westbrook, Lawrence Livermore Laboratory
10:30	Coffee break
11:00	Advances in laser diagnostics for combustion research. D. L. Hartley, Sandia Livermore Laboratory
12:00-12:45 and 2:00-5:15	DISCUSSION: Needs for High Temperature Kinetics Research Discussion Leaders: I. Glassman and F. L. Dryer Princeton University Reporters: R. F. Hampson and R. L. Brown, National Bureau of Standards

Tuesday, December 13, 1977

9:15 INVITED PAPERS

Session Chairman: O. W. Adams, DOE

Combustion Chemistry and Mechanisms.
D. M. Golden,
Stanford Research Institute

10:15 High Temperature Chemical Kinetics Data.
D. Garvin and W. Tsang,
National Bureau of Standards

11:15 Coffee Break

11:45-12:45 DISCUSSION: Acquisition of High Temperature
and Kinetic Data
1:45-4:45 Discussion Leaders: S. W. Benson,
University of Southern California
D. Gutman,
Illinois Institute of Technology
Reporters: W. Tsang and M. J. Kurylo,
National Bureau of Standards

4:45 Adjournment

Organizing Committee: O. W. Adams (DOE);
D. Garvin, L. H. Gevantman, R. F. Hampson,
and W. Tsang (NBS).

3. Commentary on the Meeting and Suggestions

W. Tsang and D. Garvin

This section is concerned with the role of chemical kinetics in combustion research. Topics considered are the types of contribution that kinetics can make, interactions between technological disciplines involved in the study of practical combustion systems, identification of some general problems and a summary of the state of the art.

The statements made here are the personal opinions of the authors. They are not a summary of agreed-upon conclusions reached at the workshop. No such summary was attempted, the belief being that information transfer among the participants should be a primary goal at this stage. But the statements have been stimulated by and draw heavily on ideas expressed at the workshop. They also incorporate material presented elsewhere. Other persons undoubtedly will wish to supplement, revise and refocus these remarks.

Combustion research and development involves much more than combustion chemistry, which, in turn, is a broader topic than combustion kinetics. The conceptual organization of the field of combustion has been analyzed by Essenhigh (ref. 1). His summary is shown in Figure 1. Although this was developed for industrial furnace technology, the translation to other combustion systems is simple. Closely analogous analyses undoubtedly hold for other practical systems that include kinetics, e.g., industrial chemical processing and air pollution control.

Three successive stages of activity are shown in Figure 1: basic sciences, technological interactions of basic sciences, and engineering systems application and development. Studies of reaction kinetics and mechanisms fall in the basic sciences stage and only begin to be applied to combustion at the technological stage, where they are combined with the outputs from other sciences. Direct interaction of kinetics with the engineering stage is not shown. Instead, the scientific results are processed via major new concepts introduced at the other stages. Inevitably, the details considered important at the basic sciences level are hidden (or lost) in the final outputs.

This leads to an appearance of strong decoupling of the sciences from the final outputs and makes it very difficult to attribute improvements at the engineering level to advances in the sciences. That this decoupling is not real is becoming apparent as detailed modeling is applied to practical combustion systems. Two conclusions from a recent modeling study bear on this point. Griffin et al. (ref. 2) modeled the fluid dynamics of the internal combustion engine. Their model included a detailed kinetic description of the chemistry. They stated:

> "The combustion process in the IC engine can be represented by finite-rate chemical reactions. The solutions are subject to inaccuracies in the rate data."

They also concluded:

> "A partial mechanism can simulate the heat process due to combustion, but the complete mechanism is required to compute the pollutants accurately."

The first quotation provides evidence of a direct influence of the scientific research on the final output. That influence would be there, although perhaps diluted and certainly hidden, in design studies that did not use explicit modeling techniques. The second speaks to an ever-present problem: simplified chemistry can be used for studies of limited scope, but different chemistry is important in different problems.

Within the discipline of chemical kinetics there is a widely held belief that detailed study of the chemistry that occurs in oxidation and pyrolysis systems (mechanisms) and quantitative data on the important elementary steps (rate constants) will be required for a satisfactory specification of combustion. That belief is valid and is supported by experience with partial solutions. It helps explain why the study of combustion kinetics is a goal in itself, independent of the consideration of practical systems. Indeed, oxidation kinetics are sufficiently complex to require the full attention of the specialists in the art. The same is true for other scientific disciplines pertinent to combustion. Thus there is a self-imposed disciplinary decoupling, in the interest of solving the "local" problems, that may be a major barrier to the development of coherent combustion research programs.

Although a detailed understanding of kinetics may be necessary for the advancement of combustion research (it certainly is not sufficient), it is not apparent that this generalized approach can be pursued rapidly enough for the results to be widely useful in technological studies. The problem is that there are many practical combustion systems and the study of them is going on in parallel with the work on kinetics. This indicates a need for establishment of priorities for kinetics studies and a need for more interdisciplinary interactions than in the past.

Nobody has solved the problem of establishment of priorities within a research community that consists of many independent small research groups, and we do not attempt to do so here. Clearly any priorities must be related to the applied problems that will be important in the near future (research takes time, impact on immediate problems is likely to be small). But priorities for scientific studies that are stated in terms of the performance of engine X or furnace Y are inappropriate and are, themselves, decoupled from the sciences. More useful priorities would cover classes of behavior applicable to several combustion systems. They could be stated in terms of needs for basic studies that would aid in the solution of identified technological problems, e.g., quench-layer kinetics in internal combustion engines, soot formation, pyrolysis in fuel droplets, pollutant formation in the oxidation of alternative fuels or ignition in aromatic hydrocarbon-air mixtures. It is then up to the kineticists to translate these needs into possible experiments, and explain what parts of the problem can be solved.

The situation is more promising with respect to interdisciplinary interaction. Most important is the direct feedback from modeling studies. Because models use detailed kinetics, and because sensitivity analyses of them can point out areas of weakness, they can indicate research needs. In addition, the explicit display of the chemistry used in the models permits the kineticist to determine whether or not that chemistry is consistent wih fundamental studies. We suggest that such analyses should be given the status of a branch of combustion kinetics.

Interpretation and simplification of kinetics for the benefit of others is another promising area of interdisciplinary work. The combustion scientist may properly ask: "which aspects of the chemistry are important in my problem and which can be ignored for the present?" The person studying spray combustion, however expert in his own field, should not be expected to be knowledgeable about reaction mechanisms or estimating rate constants. Guidance from the kineticist is desirable. One form of this is the development of simplified ("global") mechanisms. But extensive collaboration probably is required, as opposed to general guidance. We suggest that such collaborations should be promoted.

The discussion above covers general aspects of the role of kinetics in combustion. We conclude this section by listing some specific conclusions. Most of these are concerned with the state of the art within the discipline of combustion kinetics, but some touch on the general topics considered above.

1. Chemical kinetics of high temperature transformations involving hydrocarbons and related compounds are essential for the conceptualization, understanding, control and optimization of combustion devices.
2. Types of needed information range from general mechanisms to detailed single step rate constants. They cover heterogeneous as well as homogeneous phenomena and involve the oxidation and pyrolysis of aliphatic, aromatic and heterocyclic compounds. Data on pollutant formation is particularly important. These reactions cannot be decoupled from the basic combustion process.
3. Global rates constants are needed for the modeling of specific devices. They are not transferable and can be entirely empirical but preferably should be traceable to the pertinent set of single step rate constants.
4. Traditional engineering usage has place greater reliance on general mechanisms as opposed to the detailed kinetics necessary for computer simulations. The latter represents a growing research area and has enormous potentials for providing complete and general solutions and, ultimately, as an alternative to physical testing.
5. There is a serious lack of mechanistic information on the pyrolysis and oxidation of aromatic and heterocyclic systems. Thus the information for the design of combustion devices using various coal derived fuels even on a traditional basis does not exist.
6. Although the mechanisms of the oxidation and pyrolysis of aliphatic hydrocarbons are fairly well understood, large numbers of the needed rate constants remain undetermined. There is a particular need for data on hydrocarbons larger than methane.

7. There exists a vast arsenal of kinetic tools for the determination of the mechanism and rates of high temperature transformation in the gas phase. All reactions involving ground state molecules probably are accessible. There has been however no systematic effort (similar to that for stratospheric pollution) in this direction.
8. Transition state theory provides a possible framework for the extrapolation, prediction and correlation of rate parameters. Critical tests are still necessary. Particular information needs include thermal properties of unstable species as well as rate determinations.
9. In all kinetic studies proper understanding of mechanisms must precede accurate rate determinations. Particularly important is the application of a variety of experimental methodologies to the same system. Laser based techniques have great potential but there are severe limitations especially in complex systems with multiplicity of species (as in combustion). More traditional techniques, with capabilities for total analysis, e.g. gas chromatography and mass spectrometry will continue to play key roles with respect to unraveling mechanisms.
10. Computer modeling of combustion or other reactive systems is still in its infancy. There appears to be a direct need for the establishing of proper methodology in the development and extraction of information from models. Algorithms for carrying out sensitivity analysis and application to combustion systems must be developed.
11. There is essentially no capability in the combustion kinetics community for supplying detailed single step quantitative data on condensed media or multiphase reaction processes. These are research frontier areas and careful studies on model systems, with extensive aid from computer simulations will be of more lasting value than direct studies in combustion environments. At present the best that can be expected from such work is qualitative mechanistic information. Soot formation and reactions in or on soot also falls into this category. Homogeneous gas phase reactions are in general important components of these processes. Proper understanding of these processes may be a prerequisite for advances.
12. It is likely that there are too many physical properties of interest for combustion studies (rates, thermodynamic data) for all to be measured. The appropriate tactics are: (a) measure the most important, and (b) estimate the remainder.

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2. Griffin, M. D., Diwaker, R., Anderson, J. D., and Jones, E., "Computational Fluid Dynamics Applied to Flows in an Internal Combustion Engine", AIAA 16th Aerospace Sciences Meeting, 78-57. Huntsville, Alabama, January 16-18, 1978.

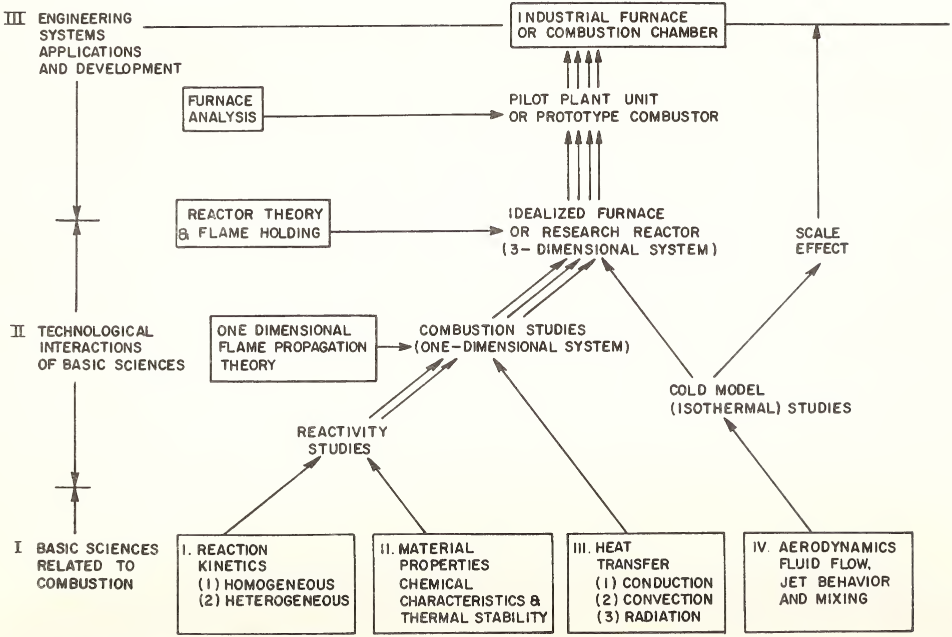

FIGURE 1. COMBUSTION SCIENCE AND TECHNOLOGY

SOURCE : R.H. ESSENHIGH

4. Abstracts of Invited Papers

COMPUTER MODELING OF COMBUSTION CHEMICAL KINETICS

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ABSTRACT

Computer modeling of chemical kinetics in combustion systems is a complex chemical, physical, and mathematical problem. In most practical applications, chemical reactions are closely coupled to other physical processes, adding further difficulties to the analysis of the chemical kinetics features of the combustion. In this paper we will try to indicate the degree of sophistication which is currently possible in numerical models of detailed chemical reaction mechanisms. We will also describe some of the methods used for simplifying or idealizing real combustion systems in order to make their analysis possible, using available numerical methods and computers. Finally, we describe what we feel are the most probable directions in which kinetic modeling for combustion applications is likely to proceed.

In addition to chemical kinetics, most combustion systems involve a variety of other physical processes, including mass and energy transport by means of either molecular diffusion or turbulent transfer. In some systems multiphase flows occur, with liquid atomization and vaporization processes in many of these situations. Radiative heat transfer may be important, and surface effects, including wall heat losses and catalytic combustion, may occur. In each large class of real combustion systems a somewhat different and distinct set of physical operators contribute to the overall system performance. Many, if not all of these physical operators are themselves extremely difficult to model computationally. In view of this degree of complexity, it is desirable to place our initial emphasis on physical systems in which chemical kinetics is the dominant physical operator. Some such systems are one dimensional laminar flames, shock tubes, and the turbulent flow reactor. These configurations are often either time-independent or spatially invariant, greatly simplifying the computational

analysis. We will show results of several computations made for laminar flame structure and propagation, as well as results of turbulent flow reactor experiment modeling for a variety of fuels.

It is our opinion that for a pure kinetics problem, a mechanism of any reasonable size can be handled numerically by available methods and computers. This capability would extend to kinetic mechanisms involving up to several hundred chemical species and many hundreds of chemical reactions. Since known reaction mechanisms are much smaller than these sizes, this statement includes any currently proposed reaction mechanisms. The computational difficulties begin to arise when spatial variations are introduced. While the pure kinetics problem might include 20 equations (species), a two-dimensional axisymmetric combustion chamber with a resolution determined by a 50 x 50 computational grid would require the solution of approximately 50 x 50 x (5 + 20) or 62500 equations for each time step. Since the computational time is required for a problem of this type depends roughly on n^2, where is the number of equations, the two-dimensional problem quickly becomes intractable. Inclusion of detailed reaction mechanisms for problems with one space dimension can be rather expensive but is possible, and some examples will be shown of stratified charge internal combustion engine studies in one space variable.

Since two- and three-dimensional geometry precludes the inclusion of detailed reaction mechanisms, it is necessary to find alternative kinetic models for these problems. We will briefly discuss a number of global, quasi-global, and semi-global reaction mechanisms in present use, some of their properties, and some examples of their use in turbulent flow reactor simulations. Several other schemes will also be discussed, including species "lumping", partial equilibrium assumptions, and partial decoupling of portions of the kinetic mechanism for species purposes.

We will discuss a number of combustion areas in which chemical kinetics are either dominant or present special problems, either in practice or with respect to their modeling. These include NOx, SOx, and soot formation, ignition processes, and catalytic combustors. In addition, we will describe a series of numerical studies of reaction quenching by a variety of physical mechanisms. These include quenching by a thermal boundary layer (wall quench), by a sharp gradient in equivalence ratio (volume quenching), and by a rapid expansion of the combustion chamber (bulk quenching).

We have attempted to indicate areas in which combustion modeling has specific needs for which kineticists may help provide solutions. Most obviously, there are a multitude of elementary chemical reactions for which rate data are unavailable or unreliable. Thermochemical data and reaction mechanisms are also needed for most practical combustion fuels. In many fuel oxidation mechanisms, kineticists could provide insight into identifying the important and rate-controlling steps. This would help in two major ways. First, it would help to validate the detailed mechanisms used in thermodynamic (0-D) and one-dimensional models. Also, it would motivate the selection of semi-global or overall steps which could be used to simplify reaction mechanisms for use in larger models. Another important function would be to indicate the degree of detail necessary , including species, elementary reactions, and reaction rates, for different applications.

We will briefly discuss coordination between modeling and diagnostics. It is important for the modeler to recognize the limitations and possibilities of experiments, including concentration, temperature, and velocity measurements. Problems exist for both types of research with respect to physical resolution, accuracy, and other properties. We see a definite value in designing idealized experiments to emphasize kinetic effects in much the same manner as noted earlier for modeling purposes. And model validation by comparison with a variety of well documented experiments is very important. We also recommend that, as part of its data base development, NBS provide critical evaluation of selected experiments which emphasize kinetic effects. These experiments can then be very useful as model validation vehicles.

We find that reaction rate data is best represented by Arrhenius coefficients. However, temperature regimes in combustion environments can vary from room temperature to over 3000 K. Many important reactions display significant non-Arrhenius behavior over this range, and it would be helpful for a data base to find a convenient way to handle this behavior within a basically Arrhenius framework. We also believe it would be very useful to maintain data for heats of formation, equilibrium coefficients of formation in both tabular and Arrhenius form, reverse reaction rates, and all manner of thermochemical data. While we realize some of this information is redundant and perhaps even formally inconsistent, it would greatly assist many modeling programs.

ADVANCES IN LASER DIAGNOSTICS FOR COMBUSTION RESEARCH

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ABSTRACT

Numerous advances have been realized in recent years in developing and applying new measurement techniques for experimental studies of combustion processes. Intrusive probes such as thermocouples and sampling probes have provided a wealth of information on combustion systems and undoubtedly will continue to do so. More recently, however, with the advent of electro-optic devices such as lasers and the rapidly developing array of detectors, techniques for measuring properties in combustion systems are being developed which do not require physically probing the experiment with a perturbing probe, but rather use some form of optical scattering to measure flow conditions.

The importance of these optical scattering techniques arises from their ability to provide excellent time response from essentially a point measurement in space as well as to overcome the limitations of physical probes. These limitations are largely related to the disturbance that they impose upon the system under study, the difficulty in surviving the hostile environment presented by combustion systems, and the difficulty in many cases of relating the measurement to properties of interest. Optical scattering techniques can be used to overcome many of these limitations for a large number of research problems.

During the last few years, several studies have been conducted by various segments of the scientific community to assess the status of optical scattering methods and to identify their limitations and the potential for extending their capabilities to problems in combustion research. In 1974, the American Physical Society conducted a summer study on the role of physics in combustion and highlighted optical diagnostics (Ref. 1). In 1975, Project SQUID conducted a workshop focused on combustion diagnostics in jet propulsion systems (Ref. 2). In 1976, the AIAA emphasized combustion diagnostics in their annual National

meeting and published special proceedings containing most of these papers (Ref. 3). In 1977 the EPA sponsored a study at United Technologies to provide a detailed review of laser techniques for practical combustion diagnostics (Ref. 4) and ERDA sponsored a study at Sandia addressing the application of these techniques to measurements in coal-fired gas turbines (Ref. 5).

To underscore the importance of optical diagnostics in combustion research, the DOE has approved the construction of a Combustion Diagnostics Facility at Sandia in Livermore, California, where several specially designed diagnostic systems will be made available for qualified users. This facility will be operational in mid-1980.

The purpose of this presentation is therefore twofold. On the one hand, this paper will introduce these techniques and their current status to the chemical kineticists in the audience who may be interested in potentially using them in their own research. On the other hand, feedback from this workshop will help formulate decisions concerning diagnostic equipment choices at the Combustion Diagnostics Facility.

Hopefully reflecting the special interests of researchers in high temperature chemical kinetics, I will limit the discussion of diagnostics to those which are capable of measuring species concentration and temperature over regimes of their interest. The techniques I will discuss are elastic Rayleigh scattering; linear inelastic scattering such as spontaneous Raman; resonant Raman and fluorescence; line-of-sight absorption; and several nonlinear optical processes including Coherent Anti-Stokes Raman Spectroscopy (CARS), Stimulated Anti-Stokes Raman Spectroscopy (SARS), Raman Induced Kerr Effect Spectroscopy (RIKES), and High Order Raman Spectral Excitation Spectroscopy (HORSES).

A brief description of field image techniques; laser shear interferometry and Ramanography, will also be presented.

In this abstract I shall discuss only a few principal scattering techniques, namely Rayleigh, Spontaneous Raman, Fluorescence and some of the nonlinear optical techniques.

Rayleigh Scattering is an elastic scattering of photons by the irradiated molecules. Being elastic, the scattered light experiences no characteristic shift in frequency, thus it can only be used to measure total number density or, by resolving the Doppler line width, may be used to measure temperature. Although of limited versatility, Rayleigh scattering has been used recently to measure temperature profiles in diffusion flames and to measure density profiles through a moving flame front. The high scattering cross-section makes Rayleigh scattering easily applied by laboratory researchers.

Raman Scattering is an inelastic process in which the scattered light has undergone a change in frequency characteristic of the internal energy levels of the irradiated molecule. For the applications discussed here, these internal modes are the vibrational and rotational energy level manifold. The intensity of light scattered at a given Raman wavelength shift (small shifts for rotational, larger shifts for vibrational) can be related directly to the number density of molecules of that particular species in the sample volume. For high -temperature gases, high molecular energy levels are populated increasingly, and the resulting distribution of intensity among Raman scattering lines is altered accordingly. Measurement of this redistribution of energy (i.e., shifts in intensity of ground-state and excited-state vibrational Raman lines) can be used to determine gas temperatures.

In compensation for the low signal strength of Raman scattering, its virtues include (1) specificity of species identity, (2) time resolution not limited by scattering process (10-14 sec), (3) accessibility of temperature information, (4) capability of probing systems not in chemical or thermal equilibrium, and (5) relative lack of interferences.

Numerous applications of spontaneous Raman scattering to combustion research have emerged in the last two or three years. Laboratory systems, including flat flames and diffusion flames, and practical systems from internal combustion engines to gas turbines have been probed with Raman systems with varying degrees of success. These results shed considerable light on the potential range of application of spontaneous Raman scattering to problems in chemical kinetics. "Typical" conclusions for Raman scattering studies at a gas turbine inlet (Ref. 5) are that in the absence of limitations due to particulates or laser- induced spectral background (both problems yet to be completely evaluated), 2σ errors of less than 10% are predicted for total measurement times of 0.02 to 0.5 seconds for all major species (N_2, O_2, CO_2, H_2O and 0.8 to 80 seconds for minor species (NO, CO, SO_2) using a conventional cw laser or advanced high- energy pulsed laser (one joule per pulse, 10 pulses per second).

Laser Fluorescence like Raman scattering, can be used as a species-sensitive optical detection method. Fluorescence techniques, using cw or pulsed tunable laser sources in principle offer the possibility of extremely sensitive detection of both atomic and molecular species. However, since fluorescence is an absorption and re-emission process, quenching and pressure broadening make data interpretation difficult. For this reason, fluorescence techniques involving saturation show greater promise since such approaches minimize the problem of quenching. Typical molecule s of interest, which have an absorption wavelength that is accessible to tunable laser sources (roughly 0.2-1.5 microns) are C_2, CH, CN, CS, NH, NH_2, NO, OH, SO_2, HCN, CH_2O, C_6H_6, and $C_{10}H_8$. Since the fluorescence cross-section s are many orders of magnitude greater than those for Raman scattering, fluorescence detection of minor species concentration is currently receiving considerable attention for combustion diagnostics.

CARS is a nonlinear optics process that recently has been shown to be of great promise as a combustion probe. CARS is a three-wave mixing process., requiring two light sources, one of adjustable frequency. For the purpose of explanation, one beam will be referred to as the pump beam at frequency w and the other as Stokes beam w_σ. These two beams are focused colinearly into the sample volume. When the frequency difference between the two beams is equal to a Raman shift for a gas in the sample volume, a coherent anti-Stokes Raman beam of frequency w_σ' is produced by the interaction with that gas.

The scattered beam is almost parallel to the incident beam and is many orders of magnitude more intense than spontaneous Raman scattering. The CARS signal, however, is no longer a simple linear dependence on laser power and number density, as is spontaneous Raman scattering. Instead, the signal is proportional to Stokes laser power, the square of the pump laser power, and the square of the density. This nonlinearity in functional dependence on input conditions places potential limitations on the application of CARS to many practical combustion environments. The work by Taran and his coworkers has addressed many of these limitations and capabilities of CARS and has been the pioneering effort to make CARS a practical system for combustion research. CARS appears to be very good for thermometry and for major species detection (>1000 ppm). For minor species, however, the probability of success is much poorer.

SARS and RIKES are other nonlinear techniques which offer relief from the intrinsic background problems of CARS. Also in contrast to CARS, these techniques do not require phase matching and the spectral output is similar to spontaneous Raman scattering and thus relatively easy to interpret. However, for both of these systems the detection apparatus can be very complex. These techniques are still in their infancy and need considerable development before their potential can be better understood.

For each of the techniques mentioned above, limitations exist which are yet to be completely resolved. Nonetheless, over the last few years, their range of applicability has been demonstrated over an increasing number of problems, and these gains are illuminated in the recent reviews referenced herein. In general, these systems are expensive ($50K to 200K) and require a trained user. The techniques are not yet developed to the point of casual application and this may never be the case. However, for the interested researcher in chemical kinetics, the problems (and risks) of setting up one of these techniques for his use are significantly lower than a few years ago. Today a number of integrated systems are in use which can be used as models and the number of knowledgeable users is greatly increased.

The Combustion Diagnostics Facility at Sandia is being organized and equipped to provide training on these optical techniques, to improve and simplify integrated diagnostic systems, and to make various techniques and state-of-the-art equipment available to users from the combustion research community.

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COMBUSTION CHEMISTRY AND MECHANISMS

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ABSTRACT

Understanding of the chemistry involved in combustion requires the general understanding of mechanisms of pyrolysis and oxidation. The object is to write a mechanism and to evaluate individual rate constants within some framework. Hopefully, this will eventually facilitate the generalization of such mechanisms for efficacy in modeling.

The framework most often employed is that of transition state theory. In this paper we will explore the validity and limitations of the use of transition state theory as a framework and suggest some possible experimental probes of the questions raised.

Experiments have been performed for many years to determine the temperature (and pressure) dependence of rate constants for elementary chemical reactions that are postulated to be important in pyrolysis and oxidation of hydrocarbons. Even though more sophisticated experimental techniques continue to become available, it will never be possible to measure all possible reactions under all possible values of temperature and pressure. This impossibility will not present us with insurmountable difficulties if we have a fundamental understanding of the nature of thermal elementary reactions which allows us to extrapolate data for specific reactions to temperature (and pressure) ranges which have not been measured, as well as to other similar reactions.

A good deal of success in establishing a framework for codification and extrapolation of rate data has been achieved with transition state theory. I will review some of the many examples where transition state theory serves as an adequate framework for rate data analysis. This will include the prediction of rate constants and their pressure and temperature dependence. We will see that critical data analysis based on transition state theory considerations has been helpful in calling our attention to systematic problems with certain experiments. Particular attention will be paid to entropy and heat capacity of activation as a criterion for understanding the details of a chemical reaction.

Thus, for example, we will review the fact that the "A-factors" for atom metathesis reactions, often available over a modest (~300-800 K) temperature range decrease for a given substrate as the reactive radical becomes progressively larger, reflecting the loss of entropy due to external degrees of freedom.

Reaction	log [A/M-1s-1]
H + C2H6	~ 11
OH + C2H6	~ 9.5
CH3 + C2H6	~ 8.5

We will also recall that abstraction of an H-atom to form a stabilized species reflects the smaller value of entropy in the transition state.

CH3 + C3H6; log [A/M-1s-1] ~ 8.0

We will discuss other examples of validity of this approach, which will include some discussion of pressure dependence of rate constants as well.

Having established the validity of the thermochemical kinetics approach, we will explore some limitations. Limitations include the fact that reported temperature dependencies for simple H-atom metathesis reactions often exceed those predicted at temperatures greater than 1000 K. On the other hand, some specific examples have recently been published of reactions with temperature dependencies that are less than predicted. Since some of these data are obtained in fairly complex experiments, there exists a strong need for direct measurements of selected reactions over a long temperature range. Experiments should give data about products as well as rate parameters because often reactions may proceed by multiple pathways. This is particularly possible at higher temperatures. Specific suggestions as to needed data will be made.

In addition, many simple reactive systems have been shown to proceed to specific product states. If this is accepted as a general characteristic of elementary processes, a legitimate question about the validity of a statistical theory, such as transition state theory, is raised. This question will also be discussed.

Finally, I will address the question of general mechanisms for oxidation and pyrolysis of aliphatic and aromatic hydrocarbons.

HIGH TEMPERATURE CHEMICAL KINETICS DATA

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ABSTRACT

A data base of reaction rate constants is needed for use in combustion research. This data base must as a start consist of rate constants for elementary thermal reactions. Data on single step reactions are applicable to all systems that may be studied whereas global rate constants are useful only in specific systems and are not transferable. Global rate constants can and should be developed from the elementary rate data base and the applicable mechanisms. State-to-state and molecular beam experiments can give valuable mechanistic information, but, today, cross sections derived from them are not easily usable in combustion problems. In time they can be folded in and guide the study of non-equilibrium aspects of combustion.

There has been a modest decline in the total number of gas kinetics measurements in recent years. But high temperature measurements (above 500 K) have decreased more sharply, limiting the growth of the combustion data base. Low temperature measurements have increased in recent years as pollution and atmospheric chemistry problems have come to the fore. One important result is that the high temperature data base is old and items in it only rarely are based on the modern higher precision experimental methods. Adaptation of these methods to high temperature kinetics is needed.

Substantial numbers of rate constants gas phase reactions have been reviewed and recommended rate constants have been published. Most of the reactions in the H2/O2 system have been reviewed. The CH4/O2 system is also reasonably well covered.

Rate constants for the overall reactions of H, O, OH, HO2 and CH3 with organic molecules have been codified, but in some cases the data are sparse and only rarely have the branching ratios been considered. Rate constants for the initial steps of pyrolysis reactions are reasonably well under control although much of the data base is old. The reviews should be updated. In contrast several classes of reactions need extensive evaluation work. Reactions of molecular oxygen have not been evaluated systematically. Processes leading to carbon formation are poorly

understood. Radical-radical combination reactions deserve more work and are getting it - both experimentally and theoretically. The outlook is promising. Radical disproportionation reactions are much less well understood and have not been systematized. The combustion scientist faces three problems in using these codified data: they are reported in many sources, they are often based on data that have large error ranges and, inevitably, exactly the reaction for which data are needed today are missing from the collections. Programs are needed that will pull together the scattered recommendations, that will provide higher precision measurements on key (sensitive) reactions and that will fill gaps in the data base by the use of estimation techniques.

It is difficult for the kineticist to determine which measurements should have high priority. Several approaches are desirable. Reactions that delineate combustion mechanisms should be studied. Even qualitative mechanistic information is very valuable. Reactions that make possible the development of correlations for classes of reactions should be emphasized. Rate constants for reactions to which models are very sensitive should be measured carefully and remeasured if older data have large errors.

The usefulness of guidance from modelling studies is indicated above. But modelling of laboratory experiments on reaction kinetics also should be fostered. Most high temperature experiments involve many elementary reactions and require elaborate interpretation of data. This can be made more reliable by modelling. The technique of sensitivity analysis should make it possible to set more realistic error limits for rate constants.

The art of data evaluation needs further development if its output - recommended rate constants - is to be reliable enough for application to combustion models. Guidance is needed from theory in order to improve judgements on the validity of data. Transition state theory and unimolecular rate theories have already proven their usefulness in the interpretation of rate constants and should be pushed to develop a framework for the techniques for extrapolation of data to different temperature and pressure regimes. They also are the starting points for the establishment of correlations among closely related reactions. Gas kineticists also have much to learn from the physical organic chemists.

Empirical and semiempirical techniques for estimating rate constants should be the subject of a major effort. They may be the answer to rapid expansion of the present data bank. The development of estimation techniques has been an active although small part of kinetics for decades. Twenty five methods have been identified. The more promising ones should be studied, validated, and their ranges of applicability determined.

While a kinetics data base for combustion studies will emphasize oxidation and pyrolysis reactions, these classes are too restrictive for present needs. Combustion kinetics is high temperature kinetics *in toto*. One must be able to handle energy release steps, to treat pollutant formation and control, to explain the behavior of additives and to meet as yet unseen needs. In addition a wide range of high temperature measurements - accurate ones - is needed to guide the theoretical developments and correlation work that will bolster the art of data evaluation.

5. Discussion of Needs in High Temperature Kinetics Research

Discussion Leaders: F. L. Dryer and I. Glassman
Princeton University, Princeton, NJ 08540

5.1 Outline for the Discussion

Many topics in this area that need to be considered by the kinetics community are listed below. This outline is intended to serve as a guide for the discussion.

A. Aromatics Pyrolysis and Oxidation Kinetics Mechanisms

1. How are these different for benzene, alkylated benzene and polynuclear aromatics? The same question must be asked about the specific problems in the following subsections.

2. Initiation and attack on aromatic ring (leading to fragmentation). Different for premixed and diffusion flames?

3. Chain branching steps - do the H2-O2 branching steps play same role as in reactions of aliphatics.

4. Production of major oxidation products - Carboxyl groups form, how? How do they break away from fragmented(?) ring, what are their fate?

5. What nitrogen fragments form and how, particularly from coal at fluidized bed temperature, what is the fate of these nitrogen fragments, what are the other competitive steps for oxygen atoms?

6. Same as 5, above, for sulfur.

B. Soot and PCAH (polycyclic aromatic hydrocarbon) Formation

1. What are the elementary processes in the gas-phase, including nucleation.

2. Does the process change with the character of the flame (pre-mixed or diffusion) for aromatics?

3. What radicals attack soot precursors most readily and how?

4. Kinetic mechanisms of soot inhibitors and promoters.

5. Is surface oxidation of soot and carbon (graphite) vastly different? Coal char? Does CO2 form at all on carbonaceous surfaces? Can it be due to catalytic effects?

6. What are the liquid-phase pyrolysis reactions leading to cenospheres? How are they affected by impurities and dissolved oxygen?

C. Overall Rate Expressions

1. Which systems hold promise for these short-cut procedures?

2. What are the limitations of this approach?

D. Sulfur Oxidation Kinetics

1. In particular, what is the mechanism of oxidative attack on organic sulfur leading to SO2?

2. Why is SO3 formation in real systems so sensitive to stoichiometry?

E. Heterogeneous Kinetics

1. Quench layer kinetics - completely obscure or well-known? Is it the region of odor (aldehyde) formation in diesels? What problems really exist in sampling probes?

2. Off-stoichiometric catalytic combustion fuel-oxygen reaction on surfaces - simply a mechanism for supply of radicals to gas phase or a mechanism for complete conversion to major products?

3. Catalytic surface combustion related to sulfur and nitrogen containing fuels.

F. Aliphatic Oxidation

1. Importance of HO2 reactions in aliphatic and CO oxidation.

2. Rate data for HO2 reactions.

3. More work on acetylene and olefin oxidation kinetic mechanism at high temperatures.

4. Oxidation in very rich mixtures - effect of O2 and H2O on pyrolysis.

G. NOx Formation and Reduction

    1. Do we already know enough about NO formation reactions?

    2. Should we not concentrate on mechanisms and rates of NO reduction reactions?

H. Thermal and Oxidation Stability of Alternative Fuels

    1. A very important medium temperature range kinetics problem.

    2. Kinetic mechanisms of in-situ combustion recovery of shale oil and other thermal and chemical secondary and tertiary recovery schemes.

I. Chemical (Homogeneous and Heterogeneous) Inhibiton of Flame Propagation

    1. Lean-limit kinetics (fuel safety problems).

    2. Anti-knock kinetics.

    3. Effect of large halocarbons molecules on lean-limit and stoichiometric combustion.

5.2 Summary of the Discussion

R.L. Brown and R.F. Hampson

The session on the first day began with the presentation of two invited papers [Chang and Westbrook, and Hartley] and a survey [Dryer and Glassman] on the needs in high temperature kinetics research. Aspects of all of these are pertinent to an understanding of the general discussion and are reviewed here.*

In the first paper Westbrook reviewed the subject of computer modeling of combustion systems. He pointed out that chemical kinetics is but one subsystem of a combustion system involving a large variety of other closely coupled physical subsystems. Modeling can be done on three levels of sophistication - subsystem modeling, parameterized modeling, and system modeling. Combustion systems are characterized by energy production by chemical reactions and the most distinctive feature is that chemical kinetics drives the system dynamics. For some systems such as one-dimensional laminar flames, shock tubes and turbulent flow reactors, chemical kinetics is the dominant physical operator. He discussed the modeling of results reported by Dryer and Glassman in the Fourteenth Symposium on Combustion for the oxidation of CO and CH4 using a turbulent flow reactor. (Reference 1) The agreement with experimental data was excellent. He also discussed the modeling of recent results on CH3OH oxidation. The conclusion reached from this purely kinetics modeling is that any reasonably sized mechanism (up to 500 reactions involving 200 species) can be handled with present day computers and computer techniques. The number of differential equations one must solve depends on the number of species and not the number of reactions. The computational problem increases dramatically when one attempts to couple the kinetics with fluid mechanics. For example, a 2-dimensional flow problem using a 50 by 50 computational grid, 5 hydrodynamic variables, and 5 chemical species requires 25000 differential equations to be solved at each time step.

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Some kind of kinetic simplification is needed to keep the computer costs within reasonable bounds. Westbrook discussed a number of alternatives to the use of detailed chemical kinetic mechanisms. These include the use of global type mechanisms. Other techniques use "lumping" methods, radical pool concepts and partial equilibrium calculations. The principle under-lying these techniques is the attempt to reduce the number of equations to be solved by replacing a differential equation by an algebraic equation. Another technique to reduce the number of equations is partial decoupling of the mechanism for trace species. He discussed a number of representative problems where chemical kinetics are crucial to an understanding of the physical system and where the solution to the problem can be said to be "kinetics information limited". These include NOx and SOx formation, soot formation, catalytic combustion, spark ignition processes, and quenching. For the application of modeling to practical combustion systems a large extension of the data base is needed. There are many important fuels, and the only one we have a good mechanism for is methane. We need detailed chemical kinetic data, reaction mechanisms, and thermo- chemical data for other fuels. Combustion problems cover an extremely wide temperature range; modelers much prefer using functional forms for temperature dependence rather than tabular data. Thermochemical data are often the hardest to obtain. In the general discussion, Westbrook (7-1) referred to the question of the coupling between kinetics and fluid flow and recommended including transport properties in a kinetics data base.

Following this talk, an opinion was expressed that most chemical kinetics shown in detailed mechanisms is irrelevant, with most systems being sensitive to a very few number of reactions. However, the majority feeling was that although a simplified mechanism can be devised to describe many systems over narrow ranges of experimental parameters, to describe them over extended ranges requires some form of detailed mechanism. There was considered to be a real need to understand chemical mechanisms and to measure rate constants for elementary reactions.

The relationship of elementary reaction rate data to the modeling of practical combustion systems received further consideration during the general discussion period. Edelson (7-2) questioned what would be the impact of the better measurement of a particular rate constant in a complex reaction scheme for a combustion model in which the chemistry is summarized in a few reactions. Engleman (7-3) pointed out three areas in which chemical kinetics can contribute to combustion research: defining the problem, expanding the data base, and arriving at a solution. Keck (7-4) recommended that laminar flame speed data be used as a critical test of the predictive capability of combustion models. It was pointed out that flame speed is directly related to flame thickness and to quench layer thickness, and that flame speed measurements are needed for practical fuels at high temperatures and high pressures. For this topic also, the view was reiterated that we must understand the basic mechanism and know the rate constants for the elementary reactions.

Dean (7-6) and Fontijn (7-8) addressed the general question of the usefulness of kinetics research. They were optimistic. Kinetics data can find quick practical application, as has been shown in rocket exhaust combustion studies, and in atmospheric pollution. The kineticist has a definite role to play. He studies the complexities of the system in order to guide the modeler in developing simplified mechanisms. Also, with an effective modeler-kineticist feedback loop emphasis can be placed on improving the critical kinetic data and the essential mechanism.

In the second invited talk, Hartley discussed advances in laser diagnostics for combustion research. He pointed out that optical scattering techniques are useful for their ability to make time dependent measurements on small regions of space without the disturbance normally introduced by physical probes. A number of techniques were discussed to introduce chemical kineticists to the possibilities of using them in their own research.

After this talk there was some discussion of whether or not the information that could be obtained by the diagnostic techniques planned for the Combustion Diagnostics Facility would be sufficient to unravel the chemistry occurring in the system. Myerson (7-5) recommended that the techniques to be used in this facility should not be restricted to those using lasers, but that other techniques, especially fast broad-spectrum infrared diagnostics should also be used.

The general discussion led by Dryer and Glassman focussed on the research needs in high temperature kinetics research. Glassman opened the discussion by noting that we know enough of the overall mechanistic characteristics of most fuels to be able to burn them efficiently. The new dimension arises from the environmental constraints that now exist. Factors such as sulfur and nitrogen emission, and soot formation have become major concerns in combustion research. A discussion outline was then presented in an attempt to concentrate attention on combustion problems considered by the discussion leaders to be important. (The detailed outline is printed immediately before this summary.) These current combustion problems were categorized as follows:

1. Aromatics - pyrolysis and oxidation.
2. Soot and polycyclic aromatic hydrocarbon formation.
3. Heterogeneous kinetics, quenching, probes, catalysis.
4. Alternative fuels - thermal and oxidative stability.
5. Sulfur oxidation kinetics.
6. NOx formation - reactions involving fuels.
7. Aliphatic oxidation - mechanism and rates.
8. Ignition, initiation and induction periods.

Apart from the topics of NOx chemistry and aliphatic oxidation, these are topics that have not been studied in detail by many kineticists. The main result of the discussion was to alert the kinetics community to the need for work in these areas.

It was generally considered that, at present, it is not possible to predict the kinetics of aromatic systems and that working out the details of the mechanism and kinetics will take perhaps a decade. However, it was felt that sufficient experimental tools are available to begin attacking the problem.

A generally similar situation was considered to exist in the area of soot formation. There are not reliable rate data for nucleation reactions. But there are strong similarities in the oxidation of soot and graphite. It was pointed out that in the combustion of some polymers, soot formation is reduced upon addition of transition metal oxides. The mechanism is unknown, but is being investigated. Fontijn (7-7) pointed out that soot formation is being studied and listed several investigators.

There was very little discussion of the subject of heterogeneous kinetics, although it was felt to be important to study heterogeneous reactions so that their effects could be differentiated from homogeneous reactions in experimental chemical systems and practical combustors.

Also there was very little discussion of the subject of alternative fuels. The point raised by the discussion leaders was that fuels derived from oil should show changes in viscosity and even solidification during storage.

The current status of our knowledge of the low temperature sulfur oxidation reactions was summarized. It was pointed out that the oxidation of divalent sulfur by O or OH begins with an addition mechanism which is known only at low temperatures and cannot be extrapolated to e.g. 2500 C. It was pointed out that the conversion of SO2 to SO3 is not yet understood.

NOx formation and reduction were the subject of considerable discussion. Bowman (7-9) emphasized that NOx emissions are kinetically limited and discussed the present state of knowledge of NO formation kinetics. He stated that we know well enough the rate constants for the reactions forming NO from atmospheric N2 (the Zeldovich mechanism) and that any inadequacy in our ability to predict the formation of NO by this mechanism is related to our inability to specify adequately the environment (temperature, O atom concentration, etc.). However, this mechanism does not predict the behavior of NO formation in fuel- rich flames or in fuels containing organic nitrogen compounds. He stressed the need for a coordinated research program in the chemical kinetics of conversion of fuel nitrogen to NOx and pointed out as specific research needs the determination of the mechanism and kinetics of the following reactions: reactions of hydrocarbon fragments (e.g., CH, CH2) with N2, the initial breakdown of fuel-nitrogen species, reactions of N-containing intermediate species (HCN, NH, NH2, CN) found in flames, reactions of NO with N-containing intermediates and fuel fragments, and lastly the suggested interaction between NOx and SOx in flames.

It was suggested that the possible attack on atmospheric N2 by the radical C2H must also be considered on the basis of a revised value of its heat of formation and newer data on the concentration of C2H2.

A recent study correlating the concentration of HCN in fuel-rich flames with the concentration of CH and CH2 was mentioned. McLean (7-10) noted that studies of the production of NO from fuel nitrogen have shown NO formation and destruction reactions to be simultaneously important.

Myerson (7-11) pointed out that the rapid reactions of these same hydrocarbon fragments with the NO produced must also be considered. Laufer (7-12) discussed results of a recent study of the reaction of CH2 with N2 indicating that formation of the spectroscopically observed HCN must proceed through a "long-lived" intermediate and is not the result of a simple reaction scheme involving N2 and either CH or CH2. In this connection, Lin (7-13) pointed out that although the direct reaction of CH with N2 to give HCN + N is "spin-hindered", this hindrance is expected to be considerably less if the intermediate complex is stable and long-lived , analogous to some O(1D) quenching reactions. Dorko (7-14) stated that research on organic nitrogen compounds is needed in order to devise methods for bypassing purification procedures.

It was generally agreed that the subject of aliphatic oxidation is not well understood; we don't even completely understand methane oxidation. In particular, the nature of formaldehyde dissociation, and methyl radical reactions with molecular oxygen needs clarification. Gelinas (7-15) felt that there is a need for simultaneous measurement of all possible flame species to yield sufficient information to allow discrimination along various chemical mechanisms.

Gann (7-16) discussed the effects of additives on combustion systems with emphasis on flame inhibition studies involving halogens and metal atoms.

In summary the main result of the first day's discussion was to point out to the kinetics community the need for fundamental research in areas not yet studied in detail.

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6. DISCUSSION OF ACQUISITION OF HIGH TEMPERATURE KINETIC DATA

Discussion Leaders: S.W. Benson, Univ. of So. California
D. Gutman, Illinois Institute of Tech.

6.1 Outline for the Discussion

The combustion of fossil fuels probably involves every category of elementary gas-phase reactions known as well as numerous heterogeneous processes. The successful modeling of practical combustion systems requires three kinds of information. First, a broad pool of general knowledge on many classes of elementary reactions is essential to have a reasonable basis for deciding which kinds of reactions should be included in the mechanism of the process under study. Second, thermochemical information on reactants, intermediates, and products is needed to calculate equilibrium constants and estimate rate constants. This information can be used to identify those reactions in the mechanism of the process under study for which accurate Arrhenius parameters are needed for reliable predictive purposes. Thirdly, for key reactions, accurate rate constants are needed at all temperatures occurring during the combustion process. Knowledge of mechanism changes with temperature as well as pressure and temperature changes in the rate constants of important unimolecular processes must also be available.

As a framework for the discussion on Acquisition of High Temperature Kinetic Data it would be useful to discuss chemical reactions important in combustion by classes defined more or less by the methods used to study them since future studies of reactions within each group will face similar experimental problems and limitations. Questions which will be raised and hopefully answered for each category of reaction should include the following:

1. Among the current means of isolating the reaction of interest for study, which provide the most useful and reliable rate constants and mechanistic information?

2. How can current methods of studying these elementary reactions be improved to be either more reliable or more accurate?

3. How can new and emerging analytical methods and experimental procedures be used to develop fresh approaches to studying these gas kinetic steps?

4. What thermochemical information is most needed to calculate Arrhenius parameters for this kind of reaction and how can it be obtained?

5. What specific reactions might have a higher priority for study in order to obtain the most useful information for practical modeling of combustion processes?

6. What value do studies performed below 500 K have for predicting mechanisms and rate constants at combustion temperatures (say 2500 K)?

7. What are "areas of exploration" which might offer new insights into various aspects of combustion including ignition, rate of heat release, formation of major pollutants (such as NO, SO2, and soot) and the formation of trace amounts of highly undesirable products?

Classes of Reactions Important in Combustion Processes

1. HIGH ACTIVATION ENERGY REACTIONS (EA>15 kcal/mole) - reactions with high activation energies control ignition delays, rates of branching, and changes of mechanism with temperature. In spite of their importance, little is known about many because such reactions must be studied at very high temperatures, often under nonisothermal conditions, and usually in systems where secondary and tertiary reactions cannot be suppressed. These reactions can be subdivided as follows:

   A. PRIMARY INITIATION - In an oxygen rich environment primary production of free-radical intermediates probably proceeds to a great extent by the reaction,

      Fuel + O2 -> 2R. (e.g. CH4 + O2 -> CH3 + HO2)

      It has not yet been possible to study such reactions directly. What information is available is largely derived from induction-time measurements in shock-heated fuel + O2 mixtures.

   B. PYROLYSIS OF MOLECULAR REACTION INTERMEDIATES - The pyrolysis of peroxides, aldehydes, and other oxygen-containing products play key rate-determining roles in low temperature combustion and in the transiton to high-temperature burning. A considerable amount of information is available from bulb experiments on the pyrolysis of larger organic molecules, and from shock-tube studies on the pyrolysis of $H2O2$ and simple hydrocarbons. Gaps in our knowledge should be identified, and the role of absolute rate theory calculations of rate constants should receive special attention.

C. PYROLYSIS OF FREE-RADICALS - The pyrolysis of chain- carriers is largely responsible for the change in combustion mechanism with temperature. Although there is some knowledge of the mechanisms, branching ratios and rate constants for the pyrolysis of alkyl radical little quantitative information is available on the rate constants for the pyrolysis of peroxy radicals (e.g. $CH3O2 \rightarrow CH3 + O2$), acyl radicals and alkoxy radicals. For many of these intermediates internal rearrangements occur at elevated temperatures complicating the kinetics picture.

Virtually all our limited knowledge of the rate constants for these processes come from indirect observations. Should special attention be directed at developing methods of detecting and directly measuring the rate constants of reactions involving polyatomic free radicals?

D. ATOM TRANSFER REACTIONS INVOLVING ALKYL RADICALS with $O2$ - Although reactions of the type,

$$R. + O2 \rightarrow \text{olefin} + HO2, \text{ and}$$

$$R. + O2 \rightarrow RO. + O$$

are known to be important in high-temperature combustion, and it is known that rate constants for these reactions are essential for combustion modeling, still essentially no quantitative information exists for either of these processes. What methods might be applied to isolate these processes for quantitative study?

2. <u>MODERATE ACTIVATION ENERGY REACTIONS</u> (2 kcal/mole$<EA<$10 kcal/mole - This category includes the chain-carrying transfer reactions responsible for heat release, some chain branching, and product formation.

A considerable body of information exists on atom-exchange involving H, and O atoms due to the ease in generating them under controlled conditions, the ability to detect these atoms at low concentrations and the fact that they can be studied in pyrex or quartz vessels or in flow reacttors. An increasing body of equally accurate information on OH-radicals is becoming available.

Most rate constant measurements do not extend above 500 K. Should more attention be directed at developing extrapolation methods to obtain high-temperature rate constants? How can accurate rate constants be measured above 500 K.

There is still a dearth of quantitative knowledge on the atom-transfer reactions of the more complex chain carriers present in the low-temperature combustion zone, reactions of alkoxy, alkylperoxy, and acyl radicals and to a lesser extent the reactions of alkyl and hydroperoxy radicals. The problem is, of course, that it is difficult to produce these intermediates under controlled conditions and also to detect them at low concentrations. Again an important question is what special methods can be developed to study reactions of polyatomic free radicals more directly and more quantitatively?

3. ADDITION AND RECOMBINATION REACTIONS (0 kcal/mole)<EA<5 kcal/mole) - addition reactions such as,

$$R + O_2 \rightarrow RO_2, \text{ and}$$

$$H;O;OH;R + \text{alkenes, alkynes} \leftrightarrow \text{Adduct} \rightarrow \text{Products}$$

are important radical-chain processes and are relatively easy to study even at room temperature because of their low activation energies. Studies of O and OH reactions with unsaturated hydrocarbons reveal the energy rich adduct can decompose in many ways, making identification of reactive routes and determination of branching ratios important. Changing Arrhenius parameters with temperature suggest mechanism changes as the temperature is raised. It would be useful to study the mechanism and rate constant changes of representative reactions from room temperature to 2500 K to provide accurate data on such transitions.

Hopefully the behavior of analogous reactions could then be calculated from the knowledge gained from such studies.

There is a large body of knowledge on the recombination rates of many free radicals, but lesser knowledge of disproportionation branching ratios and their temperature dependencies. Here again new experimental approches are needed to extend the body of knowledge in this area.

4. HETEROGENEOUS REACTIONS - The loss of free-radicals on aerosol particles early in combustion and on soot during late combustion deserves discussion. If these processes are important, how can they be quantitatively studied?

6.2 Summary of the Discussion

M. J. Kurylo and W. Tsang

The general tenor of the discussion during the second day on aquisition of kinetics data was dictated by the two invited papers [Golden, and Garvin and Tsang] and a detailed preview by the discussion leaders [Benson and Gutman] on the important classes of combustion reactions which must be attacked. In the following we summarize these talks and follow with the main points raised during the discussions.*

Golden began his review by demonstrating the immense number of reaction processes that must be known if a complete kinetic model of combustion processes is to be constructed. Exact measurement of all the reactions is clearly impossible within realistic time constraints. Thus algorithms for scaling, extrapolation, or prediction of rate parameters across reaction conditions and classes of reactants provide the only possible means of satisfying the ambitious data needs. Transition state theory using thermochemical kinetics as a calculational tool appears at present to be the only method which gives a prescription for constructing such rules. Golden illustrated its utility with applications to systems of importance in combustion contexts. He emphasized the need for supporting this approach through improved measurements on thermochemical properties of free radicals, radical termination processes, NOx formation reactions etc. Golden pointed out that although transition state theory is an equilibrium kinetic theory, RRKM calculations provide a basis for estimating departures from equilibrium behavior when energy-exchange effects are manifested in fall-offs from unimolecular behavior or in the reverse bimolecular process. He demonstrated the power of this approach with examples from atmospheric reactions and indicated that at the higher temperatures in combustion systems such effects could be expected to be much more important. Key parameters for such calculations were third body efficiencies and the structure of the transition states. Developments in these areas were summarized.

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*Statements made during the discussion are attributed to individuals only if they submitted written comments. For those cases, references are given to numbered comments in Section 7.

In the subsequent discussions the equilibrium nature of transition state theory was reiterated by several speakers. Kwei (7-17, 7-18) pointed out that inasmuch as combustion systems frequently display large departures from thermal equilibrium the entire basis for the use of such calculations under these conditions must be regarded with caution. Furthermore he noted that although transition state theory can frequently fit experimental data, questions regarding applicability and uniqueness remain. Thus uncertainties regarding predictive and extrapolative powers must still be considered. He suggested molecular beam experiments as a means of settling ambiguous points. In a similar vein the possibility of checking transition state predictions with the results of quantum mechanical calculations was presented and mention was made of such efforts on the reactions $O + CH4$ and $OH + CO$. Shaw (7-19) on the basis of his experience in correlating data on radical abstraction process recommended an empirical rate relation. Unfortunately, this formulation was at variance with transition state predictions. Skinner (7-20) was doubtful of the usefulness of the transition state approach as a predictive tool. Instead he saw a more limited role as an interpolative tool, especially among compounds of a particular class. As such it might play a particularly useful role as a basis for characterizing complex systems in terms of the reactivity of a small number of active groups. For the advocates of transition state theory the claim was made that entropies of activation could be so accurately calculated that, given a rate constant, the activation energy might frequently be calculated quite accurately. With respect to curvature in the Arrhenius plot, the suggestion was made that, since rate constants at lower temperatures are more sensitive to this effect, measurement under such conditions (< ambient) should provide a more unambiguous basis for extrapolation to higher temperatures. This is undoubtedly true, however for the large temperature ranges to be covered changes in reaction mechanisms could bring in other processes.

Finally, there was a discussion on the format for presenting the results of RRKM calculations. The general conclusion was that multiparameter fits can be easily made. However modelers indicated a preference for simple function strictly defined within limits of applicability.

Garvin and Tsang (in their paper) defined the most important elements of a combustion kinetic data base as the rate constants for elementary gas phase reactions involving the pyrolysis and oxidation of hydrocarbons and assorted pollutant related compounds at elevated temperatures.

Concentration on this type of data was due to the transferability of the information, the ubiquity of the processes in all combustion contexts and the existence of considerable information. They recognized that a complete data base should also contain state to state, heterogeneous and condensed phase data. However the underdeveloped nature of these subjects rendered their inclusion difficult. Global reactions should be derived from elementary rates. Their non-transferability suggested that inclusion in a general data base would not be worthwhile. Statistics on the production of high temperature kinetics data showed a constant or slightly declining rate during the past decade. This was in contrast with the rapid increase in measurements near ambient conditions (from pollution concerns). The successes in this area suggested that applications of the newer techniques to high temperature kinetics with a corresponding increase in activity would yield important information. Sources of evaluated kinetics data were listed and the advantages of a sole-source data base indicated. In agreement with Golden, they noted the immense volume of data needed and suggested strong experimental efforts on those reactions of importance in predictive and correlative schemes. A variety of these schemes was summarized. With respect to data accuracy, the importance of base point reactions in relative rate determinations was recognized and recommendations were made for definitive studies of these rates. The possible contributions from chemical kinetics modeling toward the building of the data base were discussed. These involved the identification of key processes and the unraveling of complex experiments. In both cases sensitivity analysis would play a key role.

The subsequent discussions focused principally on the proper use of chemical kinetics data in modeling. Many of the comments were based on participants' experiences with modeling the methane oxidation system. Some specific problems with respect to rates and mechanisms were mentioned. There was disappointment with past progress in this area and agreement that the blind use of extended lists of rate constants would not not be useful [Bauer (7-21), Myerson (7-22) and others]. Keck (7-4) suggested that useful results are not achievable in the near future, Bauer (7-21) and Gelinas (7-36) outlined possible procedures that might reduce the number of reactions considered to those which were truly meaningful. The need for proper procedures for sensitivity analysis was made clear. Gelinas (7-23) warned that reaction mechanisms may change with time regions. Indritz (7-24) pointed out that in eliminating a reaction one has set its rate constant at zero. Myerson (7-22) deplored the all too easy tendency to simply fit the data over limited ranges. Engleman (7-3) suggested that the kineticist's role should be more than supplying rate constant and that they may be able to make important contributions to problem definitions. Thus there was general agreement that the "present Laissez-faire approach which required at least two decades to home in on a reasonable mechanism for methane" Bauer (7-21) was unsatisfactory and there is a need for procedures in data analysis.

With respect to methane - oxidation the possible consequence of Golden's statement in his earlier presentation that he was unable to detect products from the CH3 + O2 reaction under Very Low Pressure Pyrolysis conditions at 1000 K was challenged by several participants on the basis of shock tube data. Possible means of reconciling the apparent conflicts were suggested. Other problem areas in the data base for methane oxidation include formaldehyde decomposition and formyl radical reactions. It was made clear that the quantitative details of the methane oxidation process remain uncertain. Finally Westley (7-25) mentioned the uncertainty in data on pyrolysis brought about by possible presence of trace quantities of oxygen.

Prior to the discussion session on high temperature data acquisition, Benson gave a general review of the interrelation of chemical kinetics, combustion and the energy crisis. In particular he highlighted the possible key roles of alkylperoxy radicals in flame propagation.

Gutman continued the discussion preview by presenting a systematic picture of the various classes of combustion related reactions that must be studied (i.e. initiation, branching, propagation, and termination). In each of the classes, the existing uncertainties far outweigh the knowns when we depart from the old familiar oxygen-hydrogen and oxygen- methane systems. He suggested, however, a variety of experimental tools which may prove useful for solving these difficult problems. Particular emphasis was placed on laser-based techniques and their possible role in the the generation, detection, and kinetic measurement of unstable polyatomic species. He challenged the experimentalists to apply the new methodology not only to rate constant measurement but to mechanistic delineation as well. Here again particular emphasis was placed on the present lack of information (or means to obtain it) on organo-peroxy and organo-oxy radicals.

Gutman stressed the importance of a careful mechanistic sensitivity analysis in the interpretation of complex experimental results. The use of a common data base for such calculation was mentioned as being a particular necessity.

Workshop participants took up the challenge of Benson and Gutmann and presented a variety of technologies which they were presently using or proposed as useful for performing high temperature combustion diagnostics and/or kinetic measurements. Many of these replies appear as written comments by the participants and are cited below.

Bauer (7-26) described some recent experiments employing a laser- Schlieren technique (post shock front density gradient technique) for making measurements on shock front gradients during the dark (induction) periods of hydrocarbon pyrolysis and oxidation. Using this method, one examines the exo-, endo- thermic balance immediately after the shock has passed through the system. A cautionary note was added that one should be concerned with gas dynamic instability due to very exothermic processes. Other comments affirmed the presently accurate temperature characterization in shock heated systems. Keck suggested a similar type of measurement facility in the spherical combustion bomb. He outlined the use of pressure transducers, ionization probes and laser diagnostics to observe flame front profiles following ignition. He further stressed (7-27) the importance of making measurements at high gas densities where many of the rate controlling processes change from trimolecular to bimolecular in character.

Tsang's recommendation (7-37) that attempts be made at minimizing the number of ongoing reactions in such systems to simplify interpretation underscored his advocacy of the single pulse shock tube technique. With such an apparatus, all but the initial reaction can be eliminated (by low reactant densities) thereby yielding very detailed mechanistic information. He suggested that under well defined initial conditions, one can "bootstrap" his way through the various stages of complexity.

These same preferences were echoed by Myerson (7-28) who envisioned the single pulse shock tube as an excellent technique for obtaining the needed kinetic data on pyrolysis and combustion of aromatic and coal- relevant molecules. In addition, he cautioned the researchers not to abandon these older methods of combustion analysis for the alluring charm of total laser diagnostics, but rather approach the problems with the full armament of measuring techniques.

Kern offered still another shock tube-associated technique in the use of time of flight mass spectrometric sampling of reflected shock zones. Such experiments have had applicability in the measurement of precursors to soot formation and the identification of chemi-ions.

Skinner (7-29, 7-30) presented an extensive list of measurement techniques and discussed their applicability for combustion studies. More specifically he, too, advocated the use of shock tube studies in order to work up gradually in the complexity of systems thereby allowing modelers to check out a complete kinetic subsystem apart from transport phenomena.

Bogan (7-31) and Seery (7-32) pointed out the versatility of molecular beam sampling mass spectrometry for probing both stable and unstable species in high temperature combustion systems. Such an apparatus coupled with optical diagnostic techniques appears useful in probing complex systems as well as studying isolated reaction processes.

Benson briefly outlined recent experiments performed using a very low pressure pyrolysis reactor for controlled free radical production. While limited in temperature range, this technique promised to be useful in getting some first data on a number of radical-radical interactions as well as radial heats of formation.

Brink's comment (7-33) solicited the inclusion of dye laser intracavity absorption as possible diagnostic for studying combustion reactions. Its high sensitivity and good spectral fidelity make it a viable candidate.

A still newer laser technique was described by Huie (7-34) who has utilized infrared multiphoton photodissociation to produce cleanly organic radicals (viz. CF2). Combination of this production technique with mass spectrometric detection should prove useful in planning controlled radical kinetic studies at high temperature.

Livingston related some recent sucess in using ESR to detect short lived free radicals produced thermally in fluids. Present capabilities allow for pressures up to 75 atmospheres and temperatures approaching 800 K.

A planned extension of the flash photolysis resonance fluorescent techniques to nearly 2000 K was described by Fontijn (7-35). The original technique has been proven to be quite versatile by many workers in measuring radical and atom reactions from 170 K to 500 K using real time fluorescence detection. Incorporation of this type facility in a furnace should permit for the first time the direct measurement of many elementary reactions at temperatures of interest to combustion modeling.

Along similar lines, the usefulness of pulsed radiolysis techniques to produce free radicals in controlled kinetics experiments was related and measurements made using this technique were summarized (7-38). Present capabilities allow pressures of up to several atmospheres. It is planned to extend the temperature capability to at least 1000 K.

7. Contributions Submitted by Participants

The participants at the meeting were encouraged to write down comments they made at the meeting and were given the opportunity to submit others afterwards. Many did so. These comments are printed in this section, aproximately in the order in which they are referred to in the summaries of the discussions, sections 5.2 and 6.2. In general, this means that comments on particular topics appear near each other. Comment references in the Summaries lead the reader to this section. An author index for this section follows the comments.

7-1

Topic: Necessary Elementary Data for Modeling.

C. Westbrook, Lawrence Livermore Laboratory. Many kinetics phenomena may be modeled from elementary rate data alone, but there are many more which are characterized by a close coupling between kinetic and spatial transport processes. In such environments observable results depend upon single particle transport rates through multicomponent gas mixtures. There is a wealth of kinetic data, which is available from good flame experimental data, but to be approached by modeling these transport coefficients must be known to within the same uncertainties as the rate data, if not better. I suggest that a proper function of a data base in this area would be to include data and evaluations on binary diffusion coefficients for different chemical species. Modelers can use this data to estimate multicomponent diffusion coefficients if necessary, but the binary diffusion coefficients into a variety of component species are needed in these transport models. Although these coefficients can be estimated from kinetic theory arguments, it is likely that molecules with many internal degrees of freedom may not diffuse in a simple way, so that experimental data are needed, and these data should be evaluated by someone who can do so properly.

7-2

Topic: Needs for High Temperature Kinetics Research.

D. Edelson, Bell Laboratories. One of the major areas of uncertainty is the relationship between fundamental chemical kinetics on the one hand and the state of the art in computer simulation of combustion systems on the other. At the present time the latter is limited to the consideration of "global" (lumped) chemical models because of the prior necessity of treating the very complex fluid and thermal transport of any real combustion system.

Because the chemistry provides the driving force for the fluid dynamics, it is not clear whether a separation of the chemical and transport computations is possible, since neither can be considered a small perturbation on the other.

In this light, it is very difficult to assess the impact which the detailed study of any particular phase of the fundamental chemistry can have on the overall problem. Beyond a qualitative grasp of the important features of the chemical mechanism, i.e., whether a class of reactions does or does not take place, it becomes questionable whether efforts at quantifying particular steps is worthwhile.

Advances in the techniques of modeling these complicated processes are required if these fragments are to be assembled into a coherent picture. New machines, and new methods in numerical mathematics are becoming available which could profitably assist in resolving these difficulties. Efforts should be made at gradually supplanting the present use of simplification and approximation methods with more exact calculations. As this is done, then a complementary requirement for improved kinetic data will become apparent, and will point the direction for future research.

7-3

Topic: Needs in High Temperature Kinetics Research.

V. Engleman, Science Applications Inc. Chemical Kineticists can make valuable contributions to combustion research in three areas:

(1) Defining the problem - identifying the key phenomena and establishing a plausible mechanism.

(2) Expanding the data base - sensitivity studies and obtaining improved kinetic information on key reactions.

(3) Arriving at a solution - narrowing down the mechanism to a tractable size and perhaps arriving at meaningful global or semi-global rate expressions, recognizing that this step is problem dependent.

Specific combustion problems are at different stages of need. Coal combustion/gasification is still at stage 1. Methane/air combustion is generally at an advanced stage 2. And portions of the methane/air combustion problem are ready for stage 3.

The kineticist should play a key role in the problem definition (stage 1) and should work closely with the modeler, especially at that stage.

It should be recognized that stage 2 is a continuing effort (improving accuracy of rate constants) and can be long-term. Stage 3 should proceed during that process.

The chemical kinetics problem is not solely in determining reaction rates even though that is an important activity. Overall problem definition and problem resolution need the guidance that can be provided by the kineticist.

7-4

Topic: Combustion Modelling

J. C. Keck, Massachusetts Institute of Technology. Among the most important combustion properties required for practical applications in engines and combustors burning premixed charges are the laminar flame speed, laminar flame thickness, wall quenching distance, ignition energy and spontaneous ignition limits at densities from roughly 1 to 100 atmospheres. The prediction of those properties from first principle is an exceedingly complex problem requiring both a knowledge of a large number of ill defined reaction rates and the numerical solution of a large system of coupled rate and diffusion equations. The probability that such a synthesis will lead to quantitatively useful (± 20%) results in the near future is extremely remote. It is therefore important that the direct measurement of the fundamental combustion properties listed above be included as an integral part of any basic chemical kinetics program related to combustion. This would serve the dual purpose of providing a critical test of the predictive capability of the synthetic approach as well as making immediately available essential information required for practical applications. In this regard it should be noted that laminar combustion properties are also useful in turbulent combustion for predicting turbulent flame thickness, ignition energy and wall quenching distance, in cases where the turbulence scale is large compared to the laminar flame thickness.

7-5

Topic: Combustion Diagnostic Facility - Infrared et al.

A. L. Myerson, Exxon. It is rather perplexing to understand why this facility which I understood was to be for general use, seems to be completely dominated by scattering techniques and/or those which use lasers. With the advent of a major stress on more complex hydrocarbons (aromatics, et al., from coal etc.), and the availability of fast, broad spectrum infrared diagnostics, at least the latter techniques should be a significant part of the facility. Other techniques should include: ARAS, laser densitometry, single-pulse shock tube analysis, etc.

7-6

Topic: Impact of Chemical Kinetics on Combustion Research.

A. M. Dean, University of Missouri-Columbia. The kineticist can provide information about the elementary chemical reactions and the associated rate constants for a particular combustion system. This information is vital to the combustion modeler even though it is often too detailed for practical combustor calculations. The importance of the mechanistic information is that, for a sufficiently detailed mechanism, it should be applicable over a wide range of conditions. The modeler can then make the necessary simplifications for his particular application and check the accuracy of his approximations against the complete mechanism. In this respect the role of the kineticist can be viewed as one who attempts to understand all the complexities of the system so that modelers can have a guide as to what constitutes a valid simplification for a given situation.

7-7

Topic: Soot Formation.

A. Fontijn, AeroChem Research Labs. Activity in this field is too low relative to its importance, but it is incorrect to state that no kinetic studies are performed.

At AeroChem Calcote and Miller are studying ionic mechanisms in soot formation. Other important activities are going on; Dr. Jack Howard at MIT and Dr. Bill Shipman at Cabot Corporation (carbon black) can give information on some of these.

7-8

Topic: When will the new kinetic data that we can generate become of practical use?

A. Fontijn, AeroChem Research Labs. Many pessimistic remarks on this subject have been made this afternoon. More optimistic notes were sounded by those involved in the stratospheric pollution problem. However, there is direct evidence as well in the combustion area that the right type of kinetic data can find quick practical application. Prime examples here are rocket exhaust combustion problems, a field of major interest ten to twenty years ago and on a lesser scale still today. Modeling studies are a common approach here and the interaction between the modelers and kineticists has paid off handsomely. The type of interaction required is, of course: (i) kineticists make their best guesses as to rate coefficients (ii) modelers incorporate these and establish which reactions are the most important, (iii) kineticists measure these, and (iv) the improved model is used by design engineers and by kineticists to determine if, and which, further reactions need study.

7-9

Topic: Chemical Kinetics of NO Formation in Combustion

C. T. Bowman, Stanford University. Environmental considerations place significant constraints on nitrogen oxide emissions from combustion systems. The trend toward use of fuels containing significant quantities of organic nitrogen compounds will make control of NOx emissions more difficult. To support development of NOx control techniques, including combustion modification and combustion gas clean-up by injection of reactive additives, a co-ordinated research program in chemical kinetics of conversion of fuel nitrogen to nitrogen oxides is required. Some specific research needs include:

1. Determination of the mechanisms of reactions between hydrocarbon fragments and molecular nitrogen. What are the reaction products? What are the relevant rate coefficients?

2. Determination of the mechanisms of initial breakdown of fuel nitrogen species. What are the reaction products? Does the relative importance of various reaction paths change in the presence of oxygen? Are there common intermediate species?

3. Determination of mechanisms and rates of reaction of nitrogen-containing intermediate species found in flames (HCN, NH, NH2, CN). These species appear to play a significant role in the NO formation process.

4. Determination of mechanisms and rates of reactions between NO and nitrogen-containg intermediates and fuel fragments. These reactions play a major role in NO removal in the flame zone and post-combustion gas.

5. Study possible interactions between NOx - SOx in flames. There is some evidence to suggest that the presence of sulfur compounds reduces NO formation from organic nitrogen compounds in flames.

7-10

Topic: NOx Formation and Reduction

W. J. McLean, Cornell University. The argument that in the fuel nitrogen problem we should emphasize studies of the NOx reduction reactions rather than the formation reactions needs some clarification. While it is true that NOx forms quite fast from fuel nitrogen, it is not necessarily true that the formation and reduction processes can be separated and studied independently. A number of studies reported in the literature indicate that the fuel nitrogen mechanism involves NO in a dual competitive reaction path. That is, NO is simultaneously being formed from some nitrogeneous intermediate and converted in part to N2 by reaction with other single-N compounds. Our own studies of NO production during HCN oxidation also indicate this general behavior, and we find NO formation and destruction to be simultaneously important in determining the eventual fate of the nitrogen.

Studies of the combined mechanisms for NO production and removal can assist combustion technologists in choosing operating stoichiometries and temperatures which maximize conversion of fuel nitrogen to N2.

7-11

Topic: Nitric Oxide Reactions for NO control.

A. L. Myerson, Exxon. Although we have discussed the importance of measuring the chemical kinetics of nitric oxide formation and destruction, as needed for NO pollution control, no mention has been made of one of the most important set of reactions in this respect. There is every evidence that no model can be made of steady-state or non-steady-state NO concentrations in hydrocarbon combustion, without considering the fast reaction of NO with hydrocarbon free radicals characteristic of the relevant flames and explosion, viz.

$$CH + NO = CHO + N$$
$$CH + NO = HCN + O$$

These are exothermic, fast, are present both early and late in hydrocarbon combustion flames and depend on the equivalence ratio for their degree of importance. They are also of considerable importance in the internal combustion engines when NO reactions with wall hydrocarbon combustion films take place reducing the NO.

7-12

Topic: Formation of NOx in Fuel-Rich Systems.

A. Laufer, National Bureau of Standards. We have examined the reaction of CH2 with N2 and directly observed the formation of HCN for which we obtained a temporal profile. The experiment involved the flash photolysis of CH2CO and analysis by vacuum ultraviolet absorption spectroscopy. HCN has a well-characterized spectrum in this region.

The major experimental observation is that HCN appears only after several hundred milliseconds following the flash. The role of CH may be eliminated both on energetic and kinetic grounds. Energetically, by the incident wavelength. Kinetically, if we use the slower of the two measured values for CH + N2, we find a 1/e time for the production of HCN of about 10 μsec - in disagreement with observation. In a like manner, we may calculate the lifetime of either 1CH2 of 3CH2 in this system to be less than 1 millisecond. Since neither of the obvious precursors can lead to HCN through a simple reaction scheme, we are required to postulate a "long-lived" intermediate which can slowly re-arrange or decompose to HCN. A complete description of this work will appear shortly in "Combustion and Flame".

7-13

Topic: Mechanism of NOx Formation.

M. C. Lin, Naval Research Laboratory. With regard to the mechanism of the CH + N2 reaction related to NOx formation, I have the following comments: (a) Although the $CH(X^2\Pi)$ + $N_2(X^1\Sigma g^+)$ -> $HCN(X^1\Sigma^+)$ + $N(^4S_{3/2})$ reaction is "spin-hindered", the hindrance (or forbiddenness) is expected to be considerably less if the reaction intermediate $H\dot{C}=N=N$ is stable and long-lived. The best examples of this are the relaxation of $O(^1D_2)$ atoms by N2 and CO. Both reactions are known to occur readily (1), although they are apparently "spin-forbidden". (b) We have previously shown (via laser emission and reaction product analyses) that the flash photolysis of CHBr3 below 200 nm generated CH in significant quantities.(2) We plan to study the reactions of CH and C2H (from BrC2H) with various molecular species of importance to combustion chemistry. An ArF laser (193 nm) will be used as a photolysis source and a dye laser for the detection of transient species. The conventional flash photolysis method is probably too slow for the CH radical because of its great reactivity and the initial long, blinding interference due to the flash.

1. R. F. Hampson and D. Garvin (Eds.)., "Chemical Kinetic and Photochemical Data from Modelling Atmospheric Chemistry," NBS Technical Note No. 866, 1975.

2. M. C. Lin, Int. J. Chem. Kinet. 6, 1 (1974); J. Phys. Chem. 77, 2726 (1973); J. Chem. Phys. 61, 1835 (1974).

7-14

Topic: NOx Formation and Reduction.

E. A. Dorko, Air Force Institute of Technology. Nitrogen-containing compounds. The mechanism, temperature, and pressure dependence of decomposition fragmentation and oxidation of nitrogen-containing organic compounds needs study to understand what occurs, in order to eliminate NOx pollutants without necessarily passing through a purification procedure (which is expensive).

In addition in the study of oxidation of aromatics, pyridine needs to be studied as an analogous, aromatic, nitrogen- containing system. At this point very little is known of these matters.

7-15

Topic: Simultaneous Measurements in Flames.

R. J. Gelinas, Science Applications. Among very high priority needs in combustion science are simultaneous measurement of major, intermediate, and minor species in flames, as a function of space and time. The emphasis should be on tractable fuels in highly interpretable simple flame systems. I am aware of only the work of Biordi and of the group at Louvain approaching this objective. Such work is necessary to provide distinctive levels of information content which will allow elementary physical and chemical mechanisms to be studied in more discriminating detail. In the absence of simultaneous measurements a superabundance of free parameters is unavoidable and the information content yields minimal discrimination of important detailed mechanisms.

7-16

Topic: Chemical Inhibition of Flame Propagation.

R. G. Gann, National Bureau of Standards. There is a need to know where the "soft" spots are in the combustion sequence, i.e., those places where a small quantity of an additive can drastically affect the global rate of fuel consumption, heat produced, etc. There is current evidence that halogen or metal atoms can be additives of this type.

If we knew how they worked, we would know how to optimize the selection of perturbing species. Thus the problem requires bulk experiments to determine specific super-additives (for a given desired effect) and to determine some character of the reactive processes involved: e.g., is the effect temperature or pressure dependent? What is the result of systematically varying the additive species, such as substituting a chlorine atom for a bromine atom or a glycol for an alcohol? With the evidence, possible competing reactions can be identified, the kinetics measured, and the magnitude of the effect corroborated (or not) by insertion into a detailed kinetic model or again by checking relative effects of two or more additives. A specific example of this involves bromine inhibition of flames. Several studies have led to the hypothesis that termolecular recombination rates are critical, and that $H + Br + M \rightarrow HBr + M$ is a specific rate constant for which we need better data to proceed further. Clearly more of this specific isolation study is needed.

In the flame inhibition field, numerous halogens, metals and organometallics have been studied and the "winners" identified. Further such studies are in progress.

7-17

Topic: Role of non-thermal process in combustion.

G. H. Kwei, Los Alamos Scientific Laboratory. I would like to offer a word of caution on the use of equilibrium rate constants in the modeling of combustion processes. Since dense mixtures of gases, many of which are reactive, are involved, it is not at all clear whether or not thermalization will precede reaction. Even if thermalization is rapid, minor channels involving non-thermal processes could be very important in pollutant formation, soot formation, and efficient combustion; such processes are clearly important in luminescence and ion-formation in flames.

Although it would be difficult to incorporate more complicated kinetics in present modeling calculations, a better understanding of the competition between energy exchange and chemical reaction and of the role of non-thermal processes is absolutely essential to our understanding of combustion processes. If we do not have this kind of information, we may be modeling the wrong system.

In order to meet this objective, we should identify a few key reactions and study (1) the dependence of the rate or cross section on reactant excitation (i.e., under non-thermal conditions) and (2) the rates or cross sections for de-excitation in collisions with molecules that are present in the combustion system.

7-18

Topic: Reliability of "Thermochemical Kinetics".

G. H. Kwei, Los Alamos Scientific Laboratory. Although Dr. Golden's inclusion of heat capacity terms in the pre-exponential factors has provided good fits to the experimental data for several reactions, it certainly is not clear that "thermochemical kinetics" would provide equally good fits for all chemical reactions or that these techniques are reliable in the extrapolation of low temperature data.

Dryer and Glassman have obtained an equally good fit for the reaction of OH radicals with CO molecules by assuming that the transition state has the same structure and vibrational frequencies as the stable HONO molecule. There are two problems with this treatment: (1) Both intuitive electronic structure theory and experimental data on the pressure dependence of the rate constant suggest that this reaction proceeds via the formation and subsequent decomposition of a long-lived complex and (2) our qualitative understanding of the electronic structures of HONO and HOCO suggest that neither the geometry nor the vibrational frequencies will be the same. Item (1) suggests that transition state theory is not applicable and item (2) suggests that even if it were applicable the quality of the fit will be affected. This raises the question of whether or not we are covering-up interesting and important features of the reaction dynamics by fitting the data to transition state models.

We are currently planning a crossed molecular beam study of this reaction as part of a larger program to study the dynamics of reactions important in combustion processes and in atmospheric chemistry. Since both the collision energy dependence and the reactant vibrational state dependence (for both reactants) of the reaction cross section will be determined, a much clearer understanding of this reaction will soon be available.

7-19

Topic: Hydrogen Transfer Reactions.

R. Shaw, Lockheed Missiles and Space Company.

Kinetics Measurements.

Rate constants for the following reactions need to be measured above 2000K:

R + CH4 = RH + CH3

where R is H, O, HO, and O2.

Kinetics Estimates.

Existing, measured, rate constants need to be fitted to k = AT2 exp (-c/t) for the reactions:

R + R'H = RH + R' (2)

where R is H, O, HO, aliphatic and aromatic and where R' is aliphatic or aromatic.

Thermochemistry.

We need more work on the heat of formation of CH3.

7-20

Topic: Correlation of Theoretical and Experimental Studies.

G. Skinner, Wright State University. At our present state of chemical knowledge it is unwise to use theoretical methods, such as Thermochemical Kinetics, RRKM theory, or more detailed theories to make long extrapolations of kinetic data (such as from experimental data at 300-600K up to 2000K) unless there are some experimental data at the high temperatures on reactions of a similar chemical type against which the theoretical method can be tested. In general, we should try to get experimental data on at least one and preferably a few specific reactions which are representative of various types (such as reactions of O atoms with secondary hydrogen atoms on fairly large hydrocarbon molecules). Once this has been done, theory can be used to obtain rate constants for other similar reactions, to fill in any unstudied temperature ranges, and to make moderate temperature extrapolations (such as 1500 - 2000K).

This approach enables us to work on the most easily studied molecules of a particular type, and therefore, to get the most accurate data, even if the easy or least difficult molecules are not those of greatest direct interest in combustion, since the theoretical methods can then fill in other molecules as needed.

It may well be possible to extend this method even further in computer modeling. If, as may be expected, the rate constants of all reactions of a given type for larger hydrocarbon molecules are about the same, the modeler may not have to consider concentrations of the large number of different molecules that may be present, but only the number of reaction centers of a given type. This may greatly reduce the number of "species" and reactions. An additional parameter such as the average number of C atoms per molecule would complete an adequate kinetic description of a collection of hundreds of different hydrocarbon molecules, such as one finds in gasoline.

7-21

General Comment, S. H. Bauer.

There is agreement that were one to model combustion processes utilizing only one or two global reactions he may arrive at misleading conclusions. At the other extreme, incorporating all of the conceivable reactions (hundreds) is definitely not practical. Professor J. Keck's rational approach merits careful scrutiny. One cannot justify on operational grounds the use of extended lists of reactions when the amount of information provided by our experimental probes is inherently limited, so that there is no feedback from the laboratory to the model builder. I find it difficult to justify (relative to combustion theory) the expenditure of great effort in obtaining for some selected reactions very precise rate constants over limited ranges of pressure and temperature, particularly when the reactions and the conditions of operation are selected on the basis of convenience. One should demonstrate that the predictions for the system's behavior are sensitive to the precise values. What is often missing is the prior selection of the reactions which should be included or omitted for each range of operations of the combustor. The crucial question which we should try to answer, is there a better strategy available than the present laissez faire approach, which required at least two decades to home-in on a reasonable mechanism for methane? In my opinion the basic components for such a strategy are available but further work is required for their integration and optimization. I submit the following:

1. For any system it is possible to list all the significant participating species--atoms, radicals, and molecules which could be present in substantial, small, or minute concentrations. This is based on our present chemical knowledge, and general "intuition".

2. For most species one can trust currently available empirical relations for estimating their enthalpies of formation and entropies.

3. It is then a straightforward calculation to estimate the equilibrium concentrations of the species listed in (1) [for any range of temperature and pressure].

4. An algorithm has been written (W. M. Shaub and S. H. Bauer: will appear in Combustion and Flame) for a computer to list all possible pairwise combinations (reactions) of the components on a list, so as to generate other members in that list, subject to atom conservation. [Ternary combinations of atoms or radicals appear as the inverse of binary dissociations].

5. For each reaction the corresponding $\Delta S, \Delta H$, ΔG are calculated.

6. All reactions for which $\Delta G > a$ (some rational positive value) are removed from the list.

7. Other simple criteria for removing unlikely reactions have been programmed, such as ΔS either very large or very negative, etc.

However, beyond this stage we encounter the practical crunch: How to program a computer so as to reduce the number of reactions (on the basis of rational kinetic criteria) from the remaining several hundred by a factor of 10. Hence at this stage we need:

(a) Empirical procedures for estimating rate constants. These must include estimates of ranges of acceptable values. Professor Benson has proposed a rational approach.

(b) Selection of critical observables for each system.

(c) Mathematical procedures for testing the sensitivity of the observables to the reactions which remain after applying steps (6) and (7), subject to the estimates in (a). For instance one may delete any reaction wherein the product of the rate constant by the equilibrium concentrations of the reactants is below some lower set limit. This can be justified on the basis of the general observation that the very reactive, unstable radicals rapidly attain local-equilibrium levels, due to the multitude of chain reactions, and then drift along with the concentrations of the major species.

Dr. Gelinas mentioned three procedures now available for making such sensitivity tests. These should be explored in detail and further developed. Since I have not used them, it is not obvious to me that any of these would be suitable when the specified error limits are large for a substantial fraction of the rate constants as listed in (a). Nevertheless, I do believe that the problem is not insoluble, provided each of us takes a hard boiled attitude regarding our favorite reactions: for any specified test we should be ready to omit any reaction which does not significantly affect the predicted observables.

7-22

Topic: Computer Modelling of Chemical Combustion Systems.

A. L. Myerson, Exxon. I believe it is incumbent upon us to encourage those who mathematically model complex chemical mechanisms of combustion to maintain a more restrictive and realistic attitude. There is absolutely no justification for including 50, 100 or even more chemical mechanistic steps, if 50% of them are uncertain by an order of magnitude, 25% by 1/2 an order of magnitude and perhaps 10% by only 50% or 100%. It is too easy to match time-dependent phenomena at one temperature. The rules of the game must be made much more stringent than that. To some extent, a more precise outlook might be engendered by adopting a "watch-dog" attitude in refereeing and reviewing processes.

7-23

Topic: Species Equilibration

R. J. Gelinas, Science Applications. The question of when individual chemical species are in local equilibrium (at a single local temperature) can be addressed by examining individual species time derivatives, $\dot{y}_i(x,t)$, which are described by differential equations of the form:

$$\dot{y}_i(x,t) = \sum_a \left\{ P_i^a(y) - L_i^a(y)y_i \right\} + T_i, \quad i=1,N$$

where P_i^a and $L_i^a y_i$ are rate expressions (of the form $k^a y$, $k^a y^2$, etc.) for individual reaction processes which produce and destroy the i^{th} chemical species at (x,t); and T_i is the local rate of transport of the i^{th} chemical species at (x,t).

For the present discussion, allow Ti to be zero or constant. One finds that, as equilibrium is approached, the individual forward and reverse reactions contained in the sets $\{P_i^a(y)\}$ and $\{L_i^a(y)y_i\}$ come into balance. This occurs over relatively long time scales. When local equilibrium is finally approached, detailed balancing is achieved between each forward and reverse process, reaction by reaction, at the local temperature $\Theta(x,t)$.

Practically, the accession to local equilibrium can be readily observed by simply rank-ordering the $P_i^a(y)$ and $L_i^a(y)y_i$ for all i species, as a function of time. At "early" times, individual forward and reverse reactions are scrambled in their order, and only a few such terms tend to constitute the $\dot{y}_i$'s. At "intermediate" times some forward and reverse reactions are seen to approach each other in rank-ordering and in individual magnitudes, and the number of processes constituting the $\dot{y}_i$'s is increasing. At large, asymptotic times, all reaction pairs (forward and reverse) balance each other and $\dot{y}_i \rightarrow 0$.

In this classic accession to equilibrium the magnitude of $\dot{y}_i$ relative to individual $P_i^a(y)$ and $L_i^a(y)y_i$ terms also undergoes a systematic progression. At "early" times $\dot{y}_i$ is of the same magnitude as a few individual $P_i^a(y)$ and $L_i^a(y)y_i$ terms. At "intermediate" times, $\dot{y}_i$ is becoming small relative to individual reaction terms ($P_i^a(y)$ and

$L_i^a(y)y_i$). In this interval $\dot{y}_i$ is generally determined by the difference of an increasing set of competing $P_i^a(y)$ and $L_i^a(y)y_i$) terms. At this stage detailed balancing has been achieved by perhaps only one or two (if any at all) individual forward and reverse reaction terms. The other reaction terms have sizeable, but offsetting, magnitudes which are still scrambled in rank-ordering. At local equilibrium $\dot{y}_i$ becomes vanishingly small relative to the individual P_i^a and $L_i^a(y)y_i$, and detailed balancing is approached, reaction by reaction, at the local temperature, $\theta(x,t)$. Even the weakest individual reactions are required to establish the final equilibrium state.

To answer the original question, it turns out for most simple combustion systems near atmospheric pressure (.01-10atm), local equilibrium is approached only at times which are very long compared to flame induction, propagation, energy deposition, and final product formation times. Thus, equilibrium rarely exists at a single temperature for most species at interesting times of flame evolution in the examples discussed today. Depending upon specific problem circumstances a fairly small number of reactions can suffice, or as many as 20-30 reactions may be needed to properly constitute the $\dot{y}_i$'s. Short-cuts are ill-advised. As a final note, it is quite possible for quasi-steady states to occur for some species at interesting flame evolution times; but this need not be synonymous with the existence of equilibrium at a single temperature. Quasi-steady state can, and does, occur when some $\dot{y}_i$ is "sufficiently small" relative to some larger scale process over specified time scales, say, τ_Q. In such cases, τ_Q may generally correspond to "intermediate" times discussed above, for which equilibrium has not yet been established at a <u>single</u> temperature. Again, the number of individual reactions needed to properly constitute the $\dot{y}_i$'s over variable time scales is very much a problem-dependent matter.

As a footnote, the concept of multiple temperatures, corresponding to effective equilibria for different species, has often been suggested in non-equilibrium physics and chemistry, but with little practical advantage being realized either conceptually or computationally.

7-24

Topic: Use of estimated rate constants in modeling.

D. Indritz, Princeton University. There is frequently criticism of the use of rate parameters that are uncertain in computer models. A point to remember is that omission of a reaction is orders of magnitude more incorrect than any reasonable estimate would be. Omission of a reaction because its rate is uncertain is effectively including a rate constant of zero - orders of magnitude off.

7-25

Topic: Aliphatic/Oxidation in Very Rich Mixtures - Effect of O2 and H2O on Pyrolysis.

E. Westley, National Bureau of Standards. I think that the "Outline of Needs" should include a statement showing clearly and explicitly the difference between non-oxidative pyrolysis and oxidative pyrolysis (= combustion). This differentiation is implicit in paragraph F4, but no where in the outline is it explicit.

Such a differentiation raises the question: How accurate is our knowledge about rate constants resulting in a closed system, completely free of any trace of O2, H2O, or any other oxygenated compound? The knowledge of non-oxidative pyrolysis is necessary to study efficiently the oxidative pyrolysis (= combustion).

7-26

Topic: CH4 Pyrolysis and Oxidation; use of Post Shock Front Density Gradient Technique.

S. H. Bauer, Cornell University. Following my brief description of the early stages of the methane pyrolysis and oxidation (fuel-rich regime):

1) Professor F. Kaufman excitedly pointed to one of my slides which showed:

$$CH4 + OH \rightarrow CH3 + H2O \qquad k = 3.00 \times 10^{13} \exp(-60{,}000/RT)$$

This is clearly a typographical error, for which I apologize. The value we used in our model was: $3.00 \times 10^{13} \exp(-6{,}000/RT)$, based on the work of Peeters and Mahnen, 14th Combustion Symposium.

2) Professor A. M. Dean questioned our use of the reaction:

$CH_2O + M = CO + H_2 + M \qquad k = 2.10 \times 10^{16} \exp(-35{,}000/RT)$

This was also taken from Peeters and Mahnen's paper. Indeed, in our complete analysis we tested the alternate route for the decomposition of formaldehyde:

$$
\begin{aligned}
&CH_2O + M \rightarrow CHO + H + M\\
&CHO + M \rightarrow CO + H + M\\
&CHO + O_2 \rightarrow CO + HO_2\\
&CHO + H \rightarrow CO + H_2
\end{aligned}
$$

When we inserted a suitable set of rate constants for these steps, essentially in agreement with the work of Schecker and Jost, which Dean favors, we found that all the computed density gradient profiles were essentially indistinguishable from those based on the single direct decomposition step. In other words, our experiments cannot discriminate between these two mechanisms.

In my brief description of the use of the psfdg technique I attempted to show its utility as a diagnostic for detailed studies of induction periods prior to the onset of ignition. I am not aware of any other experiments which provide this type of information. However, I should also add, that the conclusions derived from the density gradient profiles are limited (as is any other single diagnostic). We can make statements only with respect to reactions which either directly or indirectly (through the production of reactive intermediates) affect the thermal balance in the shock heated sample. Thus, on the basis of our data alone, we could derive no information on the role of CH_2 in the CH_4 pyrolysis, nor the detailed path for the decomposition of CH_2O. On the other hand, the need for the highly exothermic step:

$$CH_3 + O_2 \rightarrow CH_2O + OH$$

is loud and clear for T>2000 K. We underscore the need to couple several types of diagnostics for providing sharper criteria for reaction mechanisms.

7-27

Topic: High Density Kinetics.

J. C. Keck, Massachusetts Institute of Technology. In the investigation of individual reaction rates related to combustion, it is very important to include measurements at high densities, 1 to 100 atmospheres. This is the range in which the order of many of the rate controlling reactions may be expected to change from trimolecular to unimolecular in character and the assumption of bimolecular scaling is highly questionable.

7-28

Topic: Relation Between Combustion of Benzene et al. to Coal.

A. L. Myerson, Exxon. It would certainly seem that we are all basically in agreement concerning the serious need for chemical kinetic data on the combustion and pyrolysis of aromatics and other coal-relevant molecules. One technique which seems to possess considerable advantage for such research is the single-pulse shock tube.

This leads to a major point in our long-range research needs. If we are to expend considerable effort on the study of these coal-relevant molecules, a major effort will have to be made on correlating the behavior of these more tractable molecules with that of coal itself. This means that many of us will have to make side-by-side or parallel studies of coal and coal-relevant molecules under as relatable conditions as feasible.

7-29

Topic: Applicability of Various Kinetic Techniques.

C. B Skinner, Wright State University. It seems useful to make a concise list of some of the principal techniques in kinetics, with their typical applications. Seven techniques are listed below without meaning to imply that there are no others.

Technique	Application
1. Molecular beams.	Elementary reactions, often with state selection.
2. Low-pressure flow reactors.	Often useful for elementary reactions - sometimes with complications.

3. Static reactors.	Same as 2. Mainly used recently for unimolecular reactions.
4. Photochemistry.	Used to produce active species or study reactions of highly energized molecules.
5. Shock tubes.	Elementary reactions in favorable cases - more often for study of groups of reactions. A good point to model the kinetic subsystem of a complex combustion reaction.
6. High Pressure Flow Reactors.	Usually involves groups of reactions. Transport properties often of considerable importance.
7. Laminar flames.	Same as 6 - Transport properties always important, but not very hard to handle.

The methods are listed in decreasing order of the simplicity of understanding the final results (but not of carrying out the experiment). All are valuable in providing data of different types to use in combustion studies.

7-30

Topic: Role of Shock Tubes in Kinetics Research.

G. B. Skinner, Wright State University. Single elementary reactions may be studied in a shock tube under favorable circumstances. Perhaps even more important for combustion research, this technique can be used to study the net effect of groups of reactions (such as in hydrocarbon oxidation) under temperature and pressure conditions commonly reached in practical combustion processes, with minimal influences of heat and mass transfer effects and minimum wall catalytic effects. For modelers, simulation of shock tube data provides an opportunity to check out a complete kinetics sub-system before combining it with transport property sub-systems. Under some conditions, the shock tube can also be used to study wall quenching of reactions under conditions close to those in practical combustion systems.

7-31

Topic: Monitoring Radical Concentrations.

D. Bogan, Naval Research Laboratory. Development of laser assisted optical diagnostic techniques is receiving considerable attention. When these methods are (become) available for a particular species they are (will be) the methods of choice because they cause the minimum perturbation in complex chemical systems. Nevertheless, the beam sampling differentially pumped mass spectrometer is probably still the most generally useful diagnostic tool for gas phase kinetics. The most serious problem of the mass spec, i.e. extensive ion fragmentation, can be overcome by using photoionization.

High power lasers in the UV and near UV have recently become widely available. These offer the possibility of combining laser multiphoton ionization with the mass spec. Most free radicals have low lying electronically excited states and will absorb at longer wavelength than stable species which are simultaneously present in kinetic studies. Hence sensitive detection of free radicals should be obtainable with species selectivity in both the wavelength of the multiphoton process and in the mass to charge ratio of the ionized species.

7-32

Topic: 1) Needs for High Temperature Kinetics Data.
2) Acquisition of High Temperature Kinetic Data.

D. J. Seery, United Technologies Research Center.

1) One clear consensus, that seemed evident to me, was, the need for high temperature chemical kinetics studies of fuel-rich hydrocarbon oxidation. These studies of reactions such as R. + R! and R. + R'H should include both aromatic and aliphatic species.

2) The one experimental technique capable of measuring both stable and unstable species at high temperatures is molecular beam sampling - mass spectrometry. Considering the potential of this technique for studying reactive systems, it is disappointing that so few research labs are pursuing this path.

7-33

Topic: Dye laser intracavity absorption and enhancement.

G. O. Brink, SUNY-Buffalo. The possibility of the use of tunable dye laser intracavity absorption or enhancement as a diagnostic tool in combustion research should not be overlooked in the design of kinetic experiments or in the planning of the new laser diagnostic facility. We have been examining the application of this technique to the detection of atomic sodium in an atomic beam, and have detected as few as 10^6 atoms in absorption and less than 10^3 in enhancement.

At the present time the intracavity process is not understood and additional work will be required before it could be used as a routine diagnostic. However, the high sensitivity and good spectral fidelity that may be obtained make the technique potentially valuable for combustion research.

7-34

Topic: Radical Generation by CO2-TEA Laser Photolysis

R. Huie, National Bureau of Standards. Recently, J. T. Herron, W. Braun, W. Tsang and I have been working on a new method for the generation of high concentration of free radicals in a controlled manner: infrared laser photolysis. Specifically, we have used a CO2-TEA laser to produce CF2 from the photolysis of CF2HCl. The reaction CF2 + CF2 + M -> C2F4 + M was monitored using a quadrupole mass spectrometer and a rate constant derived which is in excellent agreement with the literature value. From the amount of C2F4 produced, we estimated that 140 mtorr of CF2 was produced using laser fluence of 8 J cm-2.

Not only do we feel that this method will be of great utility for the study of reactions of a large number of radicals near room temperature, we envision that the technique may allow the generation of non-equilibrium concentrations of selected radicals in flames, where their influence on flame chemistry may then be determined.

7-35

Topic: New Experimental Techniques.

A. Fontijn, AeroChem Research Labs. The need for elementary reaction kinetic data of realistic temperatures and wide temperature ranges has been implicitly emphasized frequently in this meeting. Dr. Garvin this morning mentioned our HTFFR (high-temperature fast-flow reactor) technique in which we have studied metal atom oxidation kinetics at temperatures from 300 to 1900K and pressures from 3-150 Torr. As in many hydrocarbon combustion reactions Arrhenius behavior is often not obeyed in these processes.

Under such conditions extrapolations over wide temperature ranges are not meaningful; in the Al/CO2 reaction extrapolation of the 300-700K data to 1900 K would have given a rate coefficient an order of magnitude too low (J. Chem. Phys. 67, 1561 (1977)).

The HTFFR as such appears unsuited for similar hydrocarbon combustion reaction studies because of pyrolysis problems. However, with support from DOE, Dr. Felder and I have now adapted another previously essentially low temperature technique, pulsed photolysis resonance fluorescence/absorption, to be useful for the same wide temperature range. With such an HTP (high temperature photolysis) reactor we have now initiated study of the O/CH4 reaction, to be followed by OH or O with C6H6 and O/CH3. The range of pressures which can be covered with the HTP is probably even larger than indicated above for the HTFFR; 3-760 Torr is anticipated. We suggest that once our initial studies have demonstrated the practicality of the HTP technique, it should be widely applied.

7-36

Topic: Kinetic Sensitivity Testing - A Quantitative Basis.

R. J. Gelinas, Science Applications. A recurrent phrase in this meeting has been, "What is important (chemically)?" In partial answer, I will briefly indicate an increasingly quantitative basis for importance assessments that is currently under development.

Three general axioms are well-advised in testing the importance of individual chemical reactions in flames; they are:

1. Emphasize *elementary* physical and chemical processes to the greatest *practical* extent.
2. Retention or rejection of elementary reactions is very much a problem-specific matter, in which physical and chemical mechanisms play off, relatively, against each other.
3. Resist the urge to reject candidate processes prematurely.

Each of these axioms is worthy of discussion at another time. To test kinetics mechanisms two quantitative levels of analysis are important:

.Purely kinetics sensitivity analysis

.Coupled kinetics-fluid dynamics sensitivity analysis.

Both are essential to validating a kinetics mechanism for specific applications.

The governing equations for chemical species densities, $y_i(x,t)$ (particles cm-3), are:

$$\dot{y}_i(x,t) = \sum_{\alpha} \left\{ P_i^{\alpha}(y) - L_i^{\alpha}(y) y_i \right\} + T_i, \quad i=1,N$$

where P_i^{α} and $L_i^{\alpha} y_i$ are rate expressions (of the form $k_a y$ $k_a y^2$, etc.) for individual reaction processes which produce and destroy the ith chemical species at (x,t); and T_i is the local rate of transport of the ith chemical species at (x,t).

PURELY KINETICS ANALYSIS

In purely kinetics analysis T_i is neglected. Two quantitative stages of importance testing can be exercised. The first simply rank-orders all the individual reaction terms $P_i^{\alpha}(y)$ and $L_i^{\alpha}(y) y_i$ which constitute the $\dot{y}_i$'s at all interesting problem times. Reaction rank-ordering can also be extended to energy conservation equations. It is generally found that reactions shift about in rank-ordering as time evolves. Reactions that are not important over short time scales may become important over longer time scales, etc. Examples are contained in references 1 and 2. The second quantitative stage evaluates sensitivity variables, $\partial y_i, \partial k$, which are a measure of the resultant variation in the solutions, $y_i(x,t)$, with respect to intrinsic variations (uncertainties) in the rate parameters. The time-honored method of evaluation $\partial y/\partial k$ introduces an arbitrary variation, Δk, into a given rate parameter, k, and solves the perturbed kinetic mechanism. The sensitivity is obtained from the difference quantity $[y(k+\Delta k,t) - y(k,t)]/\Delta k$. Several new computational methods (3-7) are now appearing which attempt to evaluate $\partial y/\partial k$ without repeated solutions of the kinetics mechanism. The new methods all have economical or logical problems, which have impeded widespread practical applications to the present time. Further research should resolve many of these problems.

COUPLED KINETICS-FLUID DYNAMICS ANALYSIS

For coupled analysis the magnitudes of the transport rates, $T_i\ (x,t)$, may be highly variable from one point to another in space and in time for flame systems. The transport rates, of course, depend upon gradients which are driven by the energy and momentum equations, coupled to the chemical species. Depending upon local, problem-specific conditions, fluid dynamics coupling can markedly alter the sensitivity results that would be obtained from a purely kinetics analysis. Reaction rank-ordering vis a vis, Ti, can be readily accomplished in 1-D and 2-D transient analysis operating on both species and energy equations, as a function of space and time. Only the time-honored method is currently practical for evaluating sensitivity variables, $\partial y_i/\partial k$, in 1-D or 2-D transient systems.

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7-37

Topic: Acquisition and Needs for Kinetic Data

W. Tsang, National Bureau of Standards. Single Pulse Shock tube experiments can be an excellent means of determining the mechanisms and rates of initiation in pyrolytic and many oxidative hydrocarbon decomposition systems. This is because the short reaction times < 1 msec and the low dilutions at which experiments are carried out (due to the sensitivity of gas chromatographic detectors) prevent all except the initial unimolecular decomposition processes from occurring. These same conditions permit the use of an internal standard, [a unimolecular decomposition whose rate parameters are well established] thus guaranteeing data of the highest precision and accuracy. It should be noted that these measurements are particularly suited for the derivation of correlations in rate parameters since these quantities are always compared with one another. At present sufficient data have been accumulated so as to permit derivation of the rate parameters for the initiating process (bond-breaking) in the decomposition of practically all aliphatic hydrocarbons.

With this information as a base, and with suitable adjustment of reactant concentrations measurements on the rates of many of the chain processes can and are presently being carried out. These include H and CH3 radical attack on aliphatic and unsaturates as well as branching ratios for the decomposition of alkyl radicals. It appears that the complete set of rate constants for the decomposition of aliphatic hydrocarbons to small unsaturates such as ethylene or acetylene are accessible. This in turn will set the stage for decomposition studies in the presence of increasing quantities of oxygen. The analogy here is with the work of Baldwin and coworkers where complete understanding of the H2, O2 system permit studies on the effect of added hydrocarbons.

The strategy outlined above can be easily applied to studies on aromatic and heterocyclic systems. The one fundamental problem is that of analysis. Specifically, can trace quantities of such compounds and related products be reproducibly introduced and withdrawn from a single pulse shock tube? The most obvious solution is to maintain the shock tube at several hundred degrees C. We do not believe that there are any intrinsic problems. Furthermore in view of the need for the data as outlined by Drs. Dryer and Glassman and that the same apparatus may be of use for determining the mechanism of soot-formation (through analysis of the "pre-soot"compounds that may be formed) experiments of this type would certainly appear to be worthwhile.

Finally, we note that in a more general sense the important advances in instrumentation in recent years are such that measurements can be made at increasingly shorter times, lower concentrations and on more exotic or unstable species. Thus virtually all reactions involving thermally equilibrated ground state molecules are accessible. The single pulse shock tube measurements mentioned above are a reflection of these advances. The main need is for careful systematic work with emphasis on the elementary processes.

7-38

Topic: Reactions of OH and HO_2

S. Gordon, Argonne National Laboratory.

It is clear that combustion using coal and oil as well as new fuels used in conventional and new combustion techniques is of increasing importance. Knowledge of the combustion process is therefore important in increasing the efficiency of these techniques and in designing new combustion concepts. It is well known that combustion results from a chain process involving OH and HO2 radicals which are initially produced by thermal process at rather high temperatures. The condition for ignition in the burning of fuels are such that very complex reactions involving competing, sequential, and chain branching reactions, occur in which the OH and HO2 radicals play a role.

We have the capability of studying the individual elementary reactions of these radicals under controlled experimental conditions. To date we have determined rate constants for the reactions of the OH radical with a large number of simple hydrocarbons including saturated, olefinic, and aromatic compounds as well as a number of simple inorganic compounds such as NH3, N2O, NO, NO2, SO2, and CO2. These studies were carried out at temperatures ranging from 300 to 440 K and at total pressures of reactant plus inert gas of about 1 atmosphere. We are extending our work to 600-700 K. In addition we have studied the rate constants for the following reaction:

HO2 + HO2 -> H2O2 + O2.

(k = 1.9 x 10^9 M-1 sec-1 in absence of H2O, Hamilton, J. Chem. Phys. 63, 3682 (1975).

Knowledge of the reaction rate constants for this process is vital to the understanding of combustion and atmospheric reactions involving HO2. Many rate constants have been determined for HO2 reactions in competition with the above recombination reaction. There has been a great variation in the literature on the above rate constants. We have shown that the reported discrepancies can be explained by the presence of water vapor, since the HO2 and water form a relatively stable complex which influences the rate of recombination of the HO2 radicals. We have found that NH3 has even a greater effect on this reaction. Our studies indicate that as much as 35% of atmospheric HO2 could be complexed at relatively high humidities. Another important reaction is the cross reaction between OH and HO2. There is presently an approximately 30-fold uncertainty in the rate constant for this reaction. With our 2 MeV Febetron and associated gas phase-pulse radiolysis apparatus, we have completed the experimental portion of the work on this reaction. H2O-O2-Ar (or N2) mixtures at one atmosphere were pulse radiolyzed. The decays of OH (309 nm) and HO2 (230 nm) were followed as a function of reactant concentration, dose, dose rate, total pressure and diluent gas. Our work will eliminate or substantially reduce the uncertainty in the rate constant resulting from the previously reported studies. Research has also been initiated on the reaction of HO2 with SO2. We are also extending our program to determine the reactivity of OH and HO2 with organic compounds to determine the products of these reactions. [Comment abridged, tables of rate constants omitted, Ed.]

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NBS-114A (REV. 5-78)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBS SP-531	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE Summary Report on the Workshop on High Temperature Chemical Kinetics: Applications to Combustion Research	5. Publication Date December 1978
	6. Performing Organization Code
7. AUTHOR(S) D. Garvin, R. L. Brown, R. F. Hampson, M. J. Kurylo, W. Tsang	8. Performing Organ. Report No.
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234	10. Project/Task/Work Unit No.
	11. Contract/Grant No. EA-77-A-01-0610
12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)* Department of Energy, Washington, D.C. 20545 and Office of Standard Reference Data, National Bureau of Standards, Washington, D.C. 20234	13. Type of Report & Period Covered
	14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

Library of Congress Catalog Card Number 78-600125

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The proceedings at a workshop on the applications of high temperature chemical kinetics to combustion research are summarized. This workshop, held Dec. 12-13, 1977 at the National Bureau of Standards, provided a forum for the exchange of views on the needs for kinetics research during the next five to ten years. Experimental techniques, measurements, theoretical developments and data evaluation were treated in four review papers and two discussion sessions.

This report contains the program of the meeting, abstracts of the review papers, a commentary by the organizers of the meeting, summaries of the discussions, formal comments submitted by the participants and an attendance list.

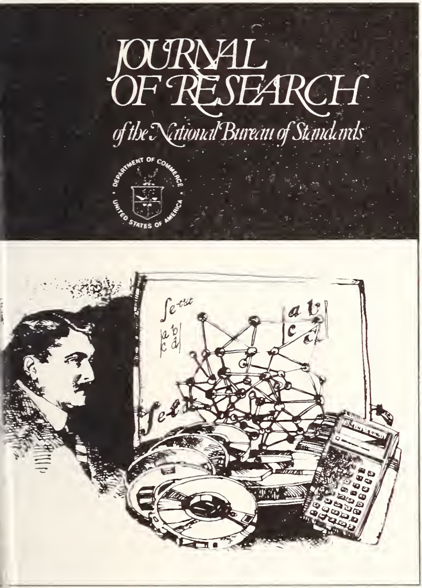
17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

chemical kinetics; combustion; high temperature chemistry; reaction rate constants; measurement techniques; assessment of needs

18. AVAILABILITY ☒ Unlimited ☐ For Official Distribution. Do Not Release to NTIS ☒ Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Stock No. SN003-003 ☐ Order From National Technical Information Service (NTIS) Springfield, Virginia 22161	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED 20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	21. NO. OF PAGES 89 22. Price $2.75

USCOMM-DC 66680-P

☆ U.S. GOVERNMENT PRINTING OFFICE: 1978 O—281-067 (337)



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