DOE/ER/13571--T1

SRI International

APR 13 1992

22 January 1991

COMBUSTION RESEARCH PROGRAM: FLAME STUDIES, LASER DIAGNOSTICS, AND CHEMICAL KINETICS

PART I: Progress Report
Covering the Period 15 July 1987 through 3 December 1990

Continuation Proposal PYU 91-012

Prepared by:

David R. Crosley, Associate Director
Molecular Physics Laboratory

Prepared for:

Department of Energy
Office of Energy Research
Division of Chemical Sciences
Germantown, MD 20545

Attn: Dr. A. H. Laufer, ER 141

SRI Project No. 2477
Grant No. DE-FG03-86ER13571

Approved:

DISCLAIMER

Donald J. Eckstrom, Director
Molecular Physics Laboratory

G. R. Abrahamson
Senior Vice President
Physical Sciences Division

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

333 Ravenswood Avenue • Menlo Park, CA 94025-3493 • (415) 326-6200 • FAX: (415) 326-5512 • Telex: 334486

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

42

PROGRESS

DE92 012575

OVERVIEW

During the past four years, we have devoted considerable effort to the quantitative detection of hydride radicals in flames, including a detailed study of the care that must be taken to correctly measure OH radical concentrations in flames. A large part of these studies has concerned collisional quenching of hydride radical species (OH, NH, and NH₂), in particular the dependence upon rotational level and collision velocity (temperature). The results on OH and NH have shown unique and interesting behavior from the viewpoint of fundamental molecular dynamics, pointing to quenching often governed by collisions on an anisotropic, attractive surface, whereas NH₂ quenching appears to depend on state-mixing considerations, not dynamic control. This state-specific behavior of these small, theoretically tractable hydrides has direct ramifications for quantitative flame diagnostics. Our other effort in the diagnostic area has been repeated but unsuccessful searches for LIF in the vinyl radical. The reaction kinetics studies have included three topics of current controversy. The first is an examination, via RRKM and transition state theory calculations, of recent, conflicting results for high temperature rate constants for OH + C₂H₄. The second is a remeasurement, using combined LP/LF and laser pyrolysis/resonance-enhanced multiphoton ionization (REMPI) detection, of the key CH₃ + O₂ reaction rate constant, which was thought to be low according to earlier measurements in our laboratory with a very low pressure photolysis (VLPΦ) apparatus but was suggested to occur by recent experiments elsewhere. The third topic is RRKM calculations on reactions of alkyl radicals and hydrogen halides, because of a controversy between results from our laboratory and that of Gutman, with serious implications for combustion chemistry.

The part of this research emphasizing flame studies is a deviation from the work proposed four years ago, in which the planned LIF development included spectroscopic studies of NH₃, HCCO, and vinyl radicals and quenching measurements on NH₂ and quenching of high rotational levels in NH. Our awareness of the need for accurate flame OH and temperature measurements prompted this substitution. In Part II of this proposal, which describes the proposed research, we include the work on NH₃ detection that was not performed under the current grant.

QUANTITATIVE LIF FLAME DIAGNOSTICS

A stringent test of the predictions from detailed computer models of flame chemistry is the profile of reactive intermediates (OH and other radicals) and the profile of the temperature (the latter profile is often critical input to the model calculation). Although qualitative insight can be obtained from relative profiles, even regions of appearance and disappearance of certain species, it is necessary to have accurate results for OH (a marker of the O/H radical pool) and the temperature.

Our experience modelling flames near 10 Torr on our low pressure burner has taught us that such highly spatially resolved flames indeed furnish critical comparisons but that considerable care must be taken to obtain results accurate enough to be meaningfully compared. Two distinct albeit closely related issues were investigated: (1) the accurate determination of OH radical concentrations, and (2) the accurate determination of a spatially resolved temperature profile. Many subtle effects producing systematic errors can occur, and these can be unnoticed if the only criterion used is statistical goodness of fit.

The experiments were performed in $\text{H}_2/\text{N}_2\text{O}$ and H_2/O_2 flames burning at 7.2 Torr pressure, on a 6-cm-diameter porous plug burner operated in an evacuated chamber. An excimer-laser-pumped dye laser of 10-ns pulse length duration excited the OH in the (0,0) band of the $\text{A}^2\Sigma^+-\text{X}^2\Pi_i$ system, and fluorescence in this same band was monitored through a 0.3-m monochromator. The resulting photomultiplier signal was fed to a transient digitizer for time decay determinations or to a boxcar integrator for temperature and concentration measurements.

To perform quantitative comparisons between flame measurements and model calculations of combustion chemistry, it is crucial to have accurate temperature measurements that are precisely spatially correlated with the species determinations. This precision is crucial because of the need to relate number density in a particular level to mole fraction and especially because of the highly nonlinear effect of temperature on a chemical reaction sequence. A systematic error of 100 or 200 K could render meaningless such comparison with a model. Flame temperatures were determined by computer-controlled rotational excitation scans in the R-branch region of the OH (A-X) 0-0 band; a prompt and narrow boxcar gate ensures that little rotational relaxation has occurred. The spectra are fit directly to two parameters: a linewidth and a temperature. This technique has been routinely applied to broadband CARS temperature measurements but has been used only once previously⁸ for LIF. Precise fits are obtained, with <3% errors (2σ) as gauged by

replicate scans over a period of months. However, systematic errors are more important for accurate measurements. These errors are due to spectral biasing⁹ against fluorescence from high N' ; the choice of gate delay, which is important because higher N' both are quenched and radiate more slowly; and flame optical depth with absorption $>5\%$.

For flame measurements at atmospheric pressure, particularly where two-dimensional imaging is desired, knowledge of the rate of collisional quenching is needed to determine the fluorescence quantum yield. Previous measurements in this laboratory have shown that values for quenching cross sections, σ_Q , for $A^2\Sigma^+ OH$ are large and vary with collider, N' , and temperature. The total quenching can probably be estimated¹⁰ to within 30% if the fuel/oxidant composition and temperature are known. Here, we measured quenching rates directly in H_2/N_2O flames. In the burnt gases, there is a slight variation with N' ; in the flame zone, the quantum yield dropped by 25%, increasing from $N' = 3$ to $N' = 8$. There was a 15% variation for mixing ratios between 0.8 and 1.5.

Spatial concentration profiles of OH were measured in the H_2/O_2 and H_2/N_2O flames, and NH was also measured in the latter flame. These profiles were compared with results from a computer model that was assembled using the Sandia flame code PREMIX¹¹ and incorporated our choices of rate constants, to help understand the responsible chemical processes and calculate the mole fractions of water, hydrogen atoms, and free radicals in the mixed oxidant flames (see below).

The H_2/O_2 flames at low pressure have an interesting behavior. The three-body chain termination reactions occur very slowly, and the flame does not reach equilibration in the chamber, with a temperature of only 1200 K many centimeters above the burner surface. Copious amounts of hydrogen atoms are produced, and these diffuse backward into the unburnt gases and decompose the reactants. OH could be observed within 1 mm of the burner surface in sufficient quantity that temperature measurements could be performed; there, the temperature was as low as 390 K. We plan to exploit this "warm" flame region in the proposed research.

The H_2/N_2O flame is terminated by bimolecular reactions and therefore goes much closer to completion, with final temperatures at 2300 K. Flames of intermediate temperatures in the burnt gases were obtained by using mixtures of the oxidants, and quenching measurements were made in these flames.

QUENCHING OF DIATOMIC HYDRIDES

Knowledge of the quenching of electronically excited states is necessary to determine the quantum yield for LIF measurements, and accordingly we have spent considerable effort on the quenching of the OH and NH radicals. These results have shown an extremely interesting and unique dependence on both rotational level and temperature that is of considerable fundamental molecular dynamic interest. Note that these species are small enough to be fully theoretically tractable, and, spurred by both our collision studies and the recent observation of OH van der Waals complexes, several groups are commencing computations of the excited state surfaces and trajectory studies of the collision dynamics.

Earlier measurements¹² on the $A^2\Sigma^+, v' = 0$ level of OH in our laboratory had shown that quenching cross sections, σ_Q , are generally large and decrease with increasing rotational level and with temperature. This points to an interaction governed by anisotropic attractive forces. Measurements on the $A^3\Pi_1, v' = 0$ level of NH have been made at elevated temperature in a laser pyrolysis/laser fluorescence system¹³ and at room temperature in a discharge flow system. For most colliders investigated at room temperature, σ_Q (NH) was found to decrease with increasing rotational level. The amount of rotational level variation was least for the most efficient quenchers (like NH_3 , with $\sigma_Q \sim 90 \text{ \AA}^2$) and more for colliders with smaller quenching cross sections. For many colliders, σ_Q decreased with temperature. Again, an anisotropic attractive surface appears to be involved, although a correlation with simple long-range attractive forces calculations is not successful as for OH.

OH quenching was measured in the burnt gas region of low pressure flames of H_2 burning mixtures of O_2 and N_2O at 7.2 Torr. Varying the oxidizer mole fraction of O_2 from 1 to 0 permitted the temperature to be varied between 1200 and 2300 K, as measured by rotational excitation scans. The burnt gases were composed of a mixture of species, mostly H_2O and N_2 for pure N_2O and mostly H_2O and H for pure O_2 , as determined by a flame chemistry model. The 10-ns pulse from a dye laser excited the OH, and the fluorescence through a small monochromator was processed by a transient digitizer. Quenching rate constants were determined by subtracting the known radiative rate from the decay rate measured at the fixed pressure. The rotational levels $N' = 3, 8$, and 16 were chosen for the laser excitation. Although some rotational relaxation occurs, most of the population is found in the initially pumped level and the molecules that have relaxed are found in levels near the initially pumped level. Thus, the quenching rate constants

measured are specific to the initially excited level and permit an examination of the temperature variation of the rotational level dependence of σ_Q . The results show clearly that the magnitude of the N' -dependence of quenching diminishes with increasing temperature: at 300 K, $\sigma_Q(N' = 3)/\sigma_Q(N' = 16) = 1.7 \pm 0.2$, while at 2300 K, the ratio is 1.02 ± 0.04 , where the room temperature results are from LIF decay measurements¹⁴ following OH production by the reaction $O(^1D) + H_2O$.

These results on the rotational level dependence of σ_Q of NH (less variation with more efficient colliders) and OH (less variation at higher temperature) can be explained within a consistent picture. The polar nature of the hydrides leads to long-range potential interaction with the colliders that is attractive and highly anisotropic, having in some orientations deep valleys that promote the formation of a transitory complex which leads to the quenching. These valleys are important for less efficient quenchers. When the radical is not rotating, it and the collider can easily find these valleys and form the complex; as it rotates, however, it averages over the surface during the approach and washes out the influence of these particularly effective regions. For an efficient collider like polar NH_3 , however, the interactions are so strong that the complex can form readily regardless of approach angle. Then the additional attraction at the preferred orientation adds little, and σ_Q is not enhanced for slowly rotating radicals as it is for the inefficient quenchers. As the temperature (collision velocity) increases, the σ_Q for each N' should decrease because of the attractive force influence. However, the σ_Q for low N' decreases faster than that for high N' because, at a higher collision velocity, the enhancement due to the preferred orientations is inhibited in the same way as it is by faster rotation.

These results raise questions about the variation of σ_Q with rotation at very high N' , currently under investigation (see below).

QUENCHING OF NH_2 RADICALS AT ROOM TEMPERATURE

The ability to observe the rotational level dependence of quenching in NH and OH depends on the fact that quenching proceeds faster than rotational thermalization; the latter is relatively slow in these molecules owing to the large level spacing. NH_2 radicals are known to quench rapidly even with He collider and therefore also appeared to be a viable candidate for a similar study. Again, NH_2 is a small molecule with theoretical tractability, although matters are considerably more complicated here than for the diatomics. A higher energy level density is caused by the added vibrations, and the ground and excited electronic states, the two components of a Renner-Teller pair, are known to perturb one another. NH_2 is a key intermediate in the chemistry of formation of NO_x and can be

detected in flames using LIF, so a study of a possible state dependence of quenching again plays a dual dynamics/diagnostics role.

The rotational level dependence of quenching of $\tilde{A}^2A_1$ NH_2 by helium was studied at room temperature in a discharge flow. The NH_2 was produced by the reaction $F + NH_3$, and fluorescence excited to three vibrational levels of the A state. The pressure dependence of the time decay of the fluorescence was used to determine the quenching cross sections. The rotational level dependence was found to vary with vibrational level: it increased regularly with N' for (0,9,0) Σ but was not significant for the neighboring (0,8,0) and (0,10,0) Π levels. This variation is probably not due to collision dynamics as for NH and OH, because each vibrational level would then behave similarly. The variation is more likely due to mixing with the ground state, which does vary with levels. However, the monotonic increase in quenching from $N' = 0$ to 7 in (0,9,0) does not correlate with a pattern from known spectroscopic perturbations. The rate constant of $2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for (0,9,0), $N' = 1$ agrees with the results of Dearden, Dixon, and Field.¹⁵

AMMONIA PHOTOLYSIS IN A JET

During the spring of 1989, D. R. Crosley spent five weeks as a visiting professor at the University of Paris (Orsay), working with P. Brechignac. The experiments conducted in Orsay were supported by the university; the analysis of the data at SRI (now underway) is supported by this project.

The experiment conducted was the 193-nm photolysis of NH_3 in a jet expansion with an Ar carrier. The experiment had two goals: (1) the determination of the rotational distribution in the ground electronic state of NH following photodissociation of cold NH_3 , and (2) the observation of NH-Ar van der Waals complexes. The data obtained show several features. NH, produced by photolysis before the expansion is complete, becomes rotationally but not vibrationally cold. A distinctly separate rotational distribution in the NH is also observed, with levels populated up to $N'' = 12$ or above. Other spectroscopic features, not due to NH, are observed in the same spectral region under certain conditions of NH_3 /Ar mixing and pressures and may be due to the complexes.

COLLISIONAL QUENCHING OF NH IN HIGH ROTATIONAL LEVELS

As noted above, quenching of NH and OH can be interpreted in terms of an anisotropic potential surface between the radical and the collider, often governed by attractive forces. An outstanding remaining question, of importance for both collision

dynamics and flame diagnostics, is the dependence of the quenching cross section σ_Q on N' for high N' . For NH, comparisons can be made between low N' and high N' distributions produced directly in the $A^3\Pi_1$ state from photodissociation of NH_3 , indicating a continued decrease above $N' = 7$, but these are not definitive. Our prior LIF studies at room temperature utilized a discharge source, producing only in lower lying rotational levels enough population to furnish adequate signals for the quenching measurements.

The studies at Orsay on photolysis of NH_3 in a jet showed that absorption of 193-nm ArF radiation produced NH radicals in high rotational levels of the ground electronic state. We have now used this method to produce NH in extremely high N' in bulb experiments. Levels up to and including $N' = 28$ have been observed in excitation scans. These levels are extremely rotationally energetic; $N' = 28$ has over $12,000\text{ cm}^{-1}$ of rotational energy.

Measurements have been made of quenching for both NH_3 and CH_4 colliders. Quantitative interpretation is complicated by the fact that translational heating of the region irradiated by the ArF laser can produce shock and rarefaction waves, although the results at low N' are in quite reasonable agreement (20%) with the room temperature discharge flow results. It is unequivocally clear, however, that the quenching cross section continues to drop with increasing N' . For NH_3 , it drops from $92\text{ \AA}^2$ at $N' = 2$ to $35\text{ \AA}^2$ at $N' = 19$ and continues to decrease for higher levels. For CH_4 , an even larger fractional decrease is found. We had anticipated that σ_Q should level off at high N' , because the anisotropies in the surface become completely averaged and further rotation would not make any difference. Consequently, very detailed dynamics effects appear to occur in these quenching collisions.

LASER-INDUCED FLUORESCENCE DETECTION OF VINYL RADICALS

Vinyl radicals, C_2H_3 , are likely participants in soot formation and the combustion of unsaturated hydrocarbon fuels. It would be extremely valuable to have LIF flame diagnostics of this radical, in addition to our recently developed capabilities for LIF detection¹⁶ for CH, singlet CH_2 , C_2H_2 , and HCO. Visible absorption has been measured by Hunziker et al.¹⁷; an origin at 499 nm is followed by a long progression of 1200 cm^{-1} to the blue, with a strong band at 423 nm. An absorption coefficient of 30 L/mol-cm was measured, indicating facile laser excitation. We thus expected that the molecule should fluoresce well. Theoretical calculations¹⁸ show that the excited state should be stable against rapid predissociation, and this was confirmed in molecular beam experiments.¹⁹

A search was made for LIF of C_2H_3 , using a low pressure discharge flow cell with various chemical schemes for the radical production. Fluorine atoms were reacted with ethylene, hydrogen atoms were added to acetylene, and direct discharges in ethylene and acetylene were examined. Conditions were selected according to current kinetics knowledge to optimize the probable vinyl concentration. Strong LIF signals were observed, but none could be attributed to vinyl. Some time was spent investigating the LIF spectrum of C_3 produced in the discharge.

The lack of success is likely due to the thermodynamic and kinetic instability of vinyl in this discharge environment. Therefore we extended our search for vinyl radical LIF, using photolytic production of the radical. The new 193-nm laser, purchased on this project and with SRI International funds, photolyzed butadiene or vinyl chloride. System sensitivity was optimized and calibrated using NH_2 LIF following photolysis of ammonia. No vinyl LIF was observed from the strongest absorption bands near 420 nm to red wavelengths at 610 nm. We can conclude that predissociation lifetimes for the strong bands are less than 10 ps, any band near 610 nm dissociates on the nanosecond time scale, and the origin of the absorption where predissociation is negligible lies farther to the red and is Franck-Condon inaccessible. (This last conclusion supports Wodtke's recent discussion.²⁰)

REACTION OF HYDROXYL RADICALS WITH ETHYLENE

RRKM and transition state theory calculations were completed on the $OH + C_2H_4$ reaction in an attempt to interpret our high temperature laser pyrolysis reaction rate data. At low temperatures the mechanism of this reaction is adduct formation. Our calculations to fit existing data provide a basis for extrapolating the pressure and temperature dependence of this channel, fix the stability of the adduct at 30 kcal/mol, and indicate that this mechanism is unimportant above 800 K. Four direct high temperature measurements have been made recently: our laser pyrolysis experiments,²¹ Tully's photolysis/LIF study,²² the pulse radiolysis work of Jonah et al.,²³ and a shock tube measurement by Bott and Cohen.²⁴ Our measurements at 850 K and 1200 K give a rate constant of $2.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The measurements made by Jonah et al.²³ and by Bott and Cohen²⁴ and our 800 K measurement are significantly higher than the other measurements. A transition state theory calculation for the expected abstraction reaction to form water and vinyl, where the barrier energy was determined from an Evans-Polanyi correlation with hydrocarbon C-H bond energies, was consistent only with the lower set of rate constant values. RRKM calculations were made for possible chemical activation rearrangement channels, but these

possibilities are incapable of accounting for the larger rate constants. In addition, possible interferences of more complex chemistry in the experimental rate measurements were examined without success. While use of the lower values is recommended, the cause of these differences remains uncertain, and more experiments focussing on real time product measurements are needed.

REACTION OF METHYL RADICALS WITH OXYGEN

A controversy as to whether the reaction

can proceed at modest temperatures had long been considered settled but has re-erupted in the recent literature.^{25,26} If this reaction proceeds easily, our understanding of the chemical nature of methane and other flames would be radically changed, since the alternative chemical fate of methyl radicals is through their self-reaction to produce higher hydrocarbons, viz:

or, at low concentrations, their reaction with other radicals such as O atoms.

We believed that an experiment in these laboratories²⁷ using the VLPP technique had shown conclusively that reaction (1) did not occur, but in light of other recent reports we set about applying some of our newer techniques to a different study of this question. We have recently begun a study using our laser pyrolysis capabilities,²⁸ along with REMPI spectroscopy of CH_3 radicals²⁹ and quantitative LIF detection of possible OH product,³⁰ to address the possibility of reaction (1).

The experiment is a modification of the LP/LF technique we developed previously during this program. In this experiment an SF_6 /bath gas (e.g., Ar, O_2) mixture is heated with an infrared laser. Unimolecular and bimolecular reactions have been studied. When bimolecular processes are studied, radicals are made by thermal decomposition of a suitable precursor (H_2O_2 for OH; $\text{CH}_3\text{N}_2\text{CH}_3$ for CH_3 , etc.). Temperature can be measured by observing various LIF rotational transitions. The reactor has been simply modified by the addition of a pair of circular electrodes. (We now have extensive experience with the REMPI technique from work on other projects.³¹) The capability to perform LIF experiments remains, now considerably augmented by the ability to measure nonfluorescing species by using REMPI. Laser pyrolysis of azomethane ($\text{CH}_3\text{N}_2\text{CH}_3$)

provides the radicals to be detected at 330 nm, which corresponds to a 2+1 REMPI process, or at 450 nm, which is a 3+1 process. We are currently characterizing radical spectra and separating the signal due to radicals from those due to shock wave effects and to probe laser ionization of the radical precursors. Thus we should shortly be in a position to follow the decay (or lack thereof) of methyl radical in the presence of oxygen in the temperature range 800-1200 K.

This work was not completed owing to lack of funds. We expect to continue these experiments under the auspices of another sponsor.

HEAT OF FORMATION OF ALKYL FREE RADICALS

The above subtitle is really a shorthand for what we perceive to be a major problem in gas phase chemical kinetics, with important ramifications for combustion chemistry. There can be no argument that values of the heats of formation of alkyl radicals are in themselves vital for quantitative understanding of the combustion of hydrocarbon fuels, but more far-reaching (see discussion below) is a current discrepancy between results in our laboratory³² and those reported by others.³³ The specific problem concerns the value and temperature dependence of the rate constant for the reactions between t-butyl radical and (H/D)X, where X = Br or I. Our value, consistent with previous measurements of the absolute rate constant of similar reactions, is almost two orders of magnitude lower than the recently reported values. In addition, where we find positive activation energies and kinetic isotope effects that would be expected for a simple metathesis reaction, others find negative activation energies.

We have performed some two-channel RRKM calculations⁶¹ that suggest a potential energy surface containing a bound intermediate of the general class $R\cdot XH$ compatible with such a negative activation energy. (This also relates, interestingly, to current DOE-sponsored studies of van der Waals complexes.³⁹) However, this model requires an intermediate bound by 8-10 kcal/mol and an inverse isotope effect. An inverse isotope effect is the opposite of the few existing observations, and such a stable complex is unexpected. Clearly a careful study of the isotope effect and temperature dependence is warranted as a search for evidence of intermediates of this type.

The reason this controversy is of such general importance is that it may suggest fundamental problems with experimental techniques that have been used to obtain a good deal of the data used in current combustion and atmospheric chemistry. Gutman and co-workers have used the same technique that yields the negative activation energies for the

R + HX processes to examine many R + O₂ reactions.³⁵ These reactions are the key to our understanding of ignition, cool flames, and product branching ratios in the oxidation of hydrocarbons. Gutman et al. have suggested values for the thermochemistry of the ensuing peroxy radicals that are different than those used previously. On the other hand, we have produced large numbers of heats of formation by the halogenation technique,³⁶ which heats depend on the value for the activation energy of R + HX reactions being small and positive. We have also measured³⁷ many radical molecule rate constants by using the technique that we call VLPΦ, which was used in the t-butyl + (H/D)X studies.

In several instances we have felt it important to comment on radical thermochemistry results suggested by other workers. This is reflected in publications 14 and 15 in our list of journal publications. The first report concerns basic errors in deriving H_xO_y thermochemistry from electrochemical potentials as done in work reported in a recent publication. The second note corrects literature values for cyclopentadienyl radical enthalpies and organometallic sandwich compounds. This interesting 5-π electron ring system has recently been implicated in the autocatalysis of methane pyrolysis.³⁸

TRANSITION STATE THEORY-BASED RATE CONSTANT ESTIMATIONS

In concert with the thought that complex chemical systems such as combustion can only be understood through a model, and given the practical impossibility of measuring all processes under conditions of interest, we continue to apply simple transition state theory (TST) to the initial estimation of many rate processes. This method is particularly applicable to simple metathesis reactions, and we have analyzed many of the reactions of this type in the methane flame model. Results are given in Table 1.

Our method, illustrated in a paper in a recent *Combustion Symposium*,³⁹ uses techniques described in Benson's *Thermochemical Kinetics*⁴⁰ to estimate transition state properties associated with the transition state entropy. Where available, we use measured values of the rate constants to establish the enthalpy of the transition state; otherwise we make estimates by analogy.

We have recently applied related TST approaches to bond scission reactions to describe the proper way to derive bond energies from pyrolysis activation energies. Care must be taken as this relationship is not simple and straightforward. This collaboration with a sabbatical visitor and renowned expert on thermochemical kinetics, Professor Alan Rodgers of Texas A&M University, is being prepared for publication.

**DATE
FILMED**

6 / 23 / 92