SAND--96-8623C

Theory and Modeling in Combustion Chemistry

CONF-960772--24

James A. Miller
Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94551-0969

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ABSTRACT

In this paper I discuss four important problems in combustion chemistry. In each case the resolution of the problem focuses on a single elementary reaction. The theoretical analysis of this reaction is discussed in some depth, with particular emphasis placed on its "unusual" features. The four combustion problems and the elementary reactions at their hearts are the following:

- 1) Burning velocities, extinction limits, and flammability limits: $H + O_2 \leftrightarrow OH + O$
- 2) Prompt NO: $CH + N_2 \leftrightarrow HCN + N$
- 3) The Thermal De- NO_x Process: $NH_2 + NO \leftrightarrow$ products
- 4) "Ring" formation in flames of aliphatic fuels and the importance of resonantly stabilized free radicals: $C_3H_3 + C_3H_3 \leftrightarrow$ products

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I. Introduction

Combustion is unique among the chemical sciences in that its study and application run the gamut of possible temperatures, pressures, and molecular sizes. As a result, the field is rich in the diversity of chemical phenomena that one may encounter routinely, both macroscopically and microscopically. Intriguing, even remarkable, chemical phenomena are associated with important practical applications in combustion. Understanding and predicting these phenomena quantitatively draw heavily on the full theoretical apparatus of gas-phase chemical kinetics, even stretching and expanding that apparatus in some cases.

In this paper and the lecture that accompanies it I want to relate to you the problems in combustion chemistry that have made the most lasting impressions on me. In each case, an important practical combustion issue is the motivating factor. Attempts to resolve this issue and to understand its origins, primarily through chemical kinetic modeling, have focused attention on a single elementary step in each case. And in each case this elementary step is shown to exhibit unexpected, somewhat unusual behavior. It is my intention to emphasize two aspects of these problems:

- 1) the relationship between the practical combustion problem and the particular elementary reaction involved, and
- 2) the theoretical analysis of the elementary reaction, our current understanding of it, and the unexpected behavior that it displays.

In the discussion below I have attempted to reach a diverse audience, from those whose primary interest is the output of combustion devices to those whose principal interest is the dynamics of molecular collisions. In so doing I have run the risk of losing both these audiences and most of the intervening spectrum. Nevertheless, I believe the potential benefits outweigh the risk. It has become clear to me that all these groups must work in concert if solutions to real problems in combustion chemistry are to be obtained.

II. The Fundamental Assumptions of Gas-Phase Reaction Rate Theory

In order to understand the interesting and unusual in chemical kinetics, it is necessary first to recognize the behavior that is normal and expected. There are three basic assumptions that underly all of gas-phase reaction rate theory:

- 1) the Born-Oppenheimer approximation,
- 2) the transition-state theory assumption, and
- 3) the RRKM, or strong-coupling, approximation.

Without these three approximations, all but the simplest of chemical reactions would be intractable theoretically.

The essence of the Born-Oppenheimer approximation is that the electrons are so much lighter than the nuclei that, during any molecular collision, they adjust their motion instantaneously to changes in the configuration of the nuclei. Consequently, one can

calculate the eigenvalues and eigenfunctions of the electronic Hamiltonian (including nuclear repulsion terms) independent of the nuclear motion. These eigenvalues (normally only the smallest ones are of interest in combustion) for all nuclear configurations of interest constitute the potential energy function that governs the nuclear motion. Thus the concept of a potential energy surface (PES) is a consequence of the Born-Oppenheimer approximation. A second consequence of the Born-Oppenheimer approximation is that the nuclear motion is adiabatic in that it conserves the quantum numbers associated with the motion of the electrons. Violations of this adiabaticity principle can occur in combustion, but normally only if there is a crossing of the potential energy surfaces. The switching of the nuclear motion from one PES to another is normally induced by very small, relativistic terms in the Hamiltonian. Consequently, chemical reactions that require a switch of potential energy surfaces are usually very slow, the weakness of the relativistic effects severely limiting their rates.

The fundamental assumption of transition-state theory (TST) (i.e. the "transition-state theory assumption") is inherently based on classical dynamics [1-5], and it is best viewed from that perspective. Quantum mechanics is inserted only after the fact to improve the accuracy of the theory by replacing the classical partition functions and sums and densities of states that appear in the rate expressions by their quantum counterparts. The only assumption required to derive classical TST is that no trajectory cross the transition-state dividing surface (TSDS) more than once.

To understand this point consider Fig. 1 (borrowed from Truhlar and Garrett [1]). In transition-state theory one computes the one-way flux of trajectories for an equilibrium ensemble (canonical, microcanonical, or microcanonical/fixed $-J$, where J is the angular momentum quantum number or its classical equivalent) through a surface in phase space (the TSDS) separating reactants from products. From an appropriate thermal averaging of these fluxes one deduces the thermal rate coefficient $k(T)$. There can be one TSDS for all conditions, one for each temperature, one for each energy E , or one for every E , J combination. If all trajectories in the type of ensemble being considered are like trajectories 1 or 4 in Fig. 1, TST rate coefficients will be exact. Further examination of Fig. 1 reveals that TST will not be exact only if there exist trajectories, whether they start as reactants or products, that cross the TSDS more than once.

These ideas lead naturally to the notion of a variational criterion [1-2] for locating the TSDS - note that the TST rate coefficient must always be too high! The "best" location then for the TSDS is the one for which the one way trajectory flux is a minimum. In principle one has enormous flexibility in specifying trial TSDS's, but in practice, these are almost always limited to multidimensional planes in configuration space that are perpendicular to the reaction path, i.e. the minimum potential-energy path connecting reactants to products. The choice of transition-state dividing surface thus is limited to a one-parameter family of such planes. If there is a significant potential energy barrier along

the reaction path, a single TSDS located at the top of the barrier is normally an excellent choice for all conditions. However, if there is no potential-energy barrier, as is the case for radical-radical reactions for example, one must make use of the variational criterion explicitly. Normally the more constraints we place on the choice of the TSDS, the more accurate is the resulting rate coefficient, i.e. canonical variational theory (CVT, one TSDS for each temperature) is less accurate than microcanonical variational theory (μ VT, one TSDS for each E), and μ VT in turn is less accurate than microcanonical/fixed -J variational theory (μ VT-J, one TSDS for every E, J combination). Excellent discussions of transition-state theory from a dynamical point of view, including mathematical derivations of the rate expressions, are given in the references cited above and in the book by Gilbert and Smith [6].

The RRKM approximation is perhaps the most intriguing, and the most difficult to grasp, of the three fundamental assumptions listed above. It applies to highly excited molecules or collision complexes and, like transition-state theory, is most fruitfully viewed from a classical-mechanical perspective. However, unlike TST, the uncertainty principle probably makes the RRKM assumption more valid quantum mechanically than classically. In classical terms the RRKM assumption says that the degrees of freedom of a highly excited, isolated molecule (or collision complex) are so strongly coupled that, no matter how "locally" in phase space an ensemble of such molecules is prepared, on a time scale much smaller than the characteristic time for reaction, this ensemble will evolve to fill the complete phase space available to it (consistent with conservation of energy and angular momentum). Reaction thus always takes place from a microcanonical/fixed-J ensemble (sometimes approximated simply by a microcanonical ensemble). This is shown schematically in Fig. 2. The motion thus may be described as "chaotic," with the ensemble constantly adjusting so that the distribution of complexes is always uniform over the accessible phase space. The RRKM assumption is expected to become better as the number of atoms involved in the motion increases and as the depth of the potential well over which the reaction takes place becomes greater.

A consequence of the RRKM assumption is that, no matter how energy is deposited in a molecule, the same reaction rates result. It is thus possible to define universal rate coefficients $k(E, J)$, or $k(E)$. A large number of such molecules then will have a lifetime distribution that is exponential with a $1/e$ decay time (or lifetime) of $1/k(E, J)$. Bunker and Hase [7] and Hase [8] discuss the dynamical implications of RRKM and non-RRKM behavior at some length, paying particular attention to the effects on lifetime distributions of non-RRKM behavior.

I shall have occasion to refer extensively to all three of these theoretical idealizations in the discussions that follow.

III. Burning Velocities, Extinction Limits, and Flammability Limits - The $H + O_2 \leftrightarrow OH + O$ Reaction

The chain-branching reaction between hydrogen atoms and oxygen molecules,

is ubiquitous in combustion. Any time we want to know whether or not a gas mixture will burn or how fast it will burn, reaction (R1) is primarily responsible for determining the outcome. Some illustrations are in order.

Figure 3 is a sensitivity diagram for burning velocities of methane-air mixtures at atmospheric pressure. By far the largest positive sensitivity coefficient is that for reaction (R1), indicating that increasing k_1 (the rate coefficient for (R1)) will increase the rate at which the flame propagates more than any of the other reactions in the mechanism. Moreover, the sensitivity coefficients for the other reactions can be understood from their relationship to (R1). Generally, any reaction that helps produce H atoms, either directly or indirectly, has a positive sensitivity coefficient, and any reaction that hinders hydrogen atom formation has a negative sensitivity coefficient. The H atoms then react with O_2 via (R1). Thus reactions such as

have large positive sensitivity coefficients, and reactions such as

have large negative sensitivity coefficients. A somewhat less obvious example is reaction (R9),

which has a negative sensitivity coefficient because it competes for HCO with (R3), which is a primary source of hydrogen atoms.

The same theme is at work when we consider flame extinction. Counterflow flames are an important source of information (both experimentally and theoretically) about the effects of external flow fields on laminar flames, both premixed and non-premixed. Such flames can be extinguished by "flame stretch," an important practical phenomenon [9]. Kee, et al. [10] have shown that extinction in such premixed flames occurs when the residence time in the reaction zone drops to the point where (R1) cannot produce free radicals at a sufficiently rapid rate to sustain combustion. Near extinction the maximum flame temperatures have large positive sensitivity coefficients for reaction (R1) and for reactions that produce H atoms and large negative sensitivity coefficients for reactions that consume hydrogen atoms in competition with (R1). Extinction in stirred reactors and diffusion flames occurs the same way.

Due largely to the work of Law and Egolfopoulos [11, 12], our understanding of flammability limits in gases has improved dramatically in the last few years. Such limits

have been puzzling because calculations of freely propagating, adiabatic flames show that such flames have no limits! Thus it would appear that flammability limits must depend crucially on boundary conditions, a conclusion that is contradicted by a sizable body of experimental data that shows the same limits to be obtained in different measurement devices. The latter result implies that flammability limits are fundamental properties of gas mixtures.

Law and Egolfopolous have explained this apparent contradiction and proposed a kinetic criterion for obtaining rich and lean limits from adiabatic flame calculations. From a sensitivity analysis one first identifies the primary "chain-branching" and "chain-termination" reactions; in principle they could be different for lean and rich mixtures. In practice, for normal fuels burning in oxygen or air the primary chain-branching step is always (R1), and under lean conditions the primary chain-termination step is always (R6). The second reaction actually need not be chain terminating; it is simply the reaction that competes most favorably with (R1) for hydrogen atoms, and normally it is different for different fuels under rich conditions. The flammability limit is identified as the equivalence ratio ϕ at which the maximum rate of (R1) and the maximum rate of its primary competitor are equal. The basic idea is that under such conditions flame propagation becomes tenuous, and very small amounts of heat transfer or irregularities in the flow field ahead of the flame can cause flame propagation to cease. If radiative heat transfer from the burned gases to the unburned gases is included in the calculation, flame propagation indeed does not exist past the conditions just described, and the flammability limits become fundamental properties of the gas mixtures, i.e. independent of boundary conditions.

One can see from this discussion that the same concept is at work in determining flammability limits as in determining burning velocities and extinction limits, i.e. the competition between (R1) and other reactions for H atoms. One might improve on the Law-Egolfopolous method by including all competing reactions, but the present method appears to work well. In general, at the flammability limit not only are the peak rates of (R1) and its competitor equal, but the peaks also occur at the same place in the flame. Thus one may construct a plot such as Fig. 4, in which the temperatures in the flame at which the pertinent peak rates occur are plotted versus O_2 level for a methanol/CO-oxygen flame diluted in CO_2 , and identify the flammability limit as the intersection of the curves.

From the foregoing discussion it should be clear that reaction (R1) is of overwhelming importance in combustion. The reverse reaction,

is also important in atmospheric chemistry. Consequently, reaction (R1) has been studied extensively both experimentally and theoretically in both directions [13], and its rate coefficient is known to an accuracy of approximately $\pm 20\%$ over the very wide range of temperatures, $250 \text{ K} < T < 5300 \text{ K}$ [13]. In this statement and in the discussion that

follows it is assumed that k_1 and k_{-1} can always be related through the equilibrium constant, i.e. $k_1/k_{-1} = K_{eq}$.

Even though reaction (R1) looks quite harmless at first glance - just three atoms with one bond breaking and one new bond forming, theoretically it shows some unexpected dynamical behavior. To understand this behavior, first consider the reaction coordinate diagram shown in Fig. 5. The most important features of the PES shown in the diagram are that the reaction takes place over a deep potential well corresponding to the HO_2 molecule, it is significantly exothermic ($\sim 17\text{kcal/mole}$) if viewed from the reverse direction, and there are no potential energy barriers in either the O-OH entrance channel or the H - O_2 exit channel. The dynamical features of interest are best understood if we consider the reaction in the $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ direction. Consequently, I take this point of view almost exclusively in the following discussion.

About ten years ago [14] I was using quasi-classical trajectories (QCT) on the Melius-Blint PES [15] to determine k_{-1} when I discovered that a very large number of trajectories entered the HO_2 well region of the potential and, after undergoing at least one O - O inner turning point, subsequently redissociated to $\text{O} + \text{OH}$, close to 50% even at temperatures as low as 200 K. The number increased to 70% at 2500 K. On the basis of RRKM theory (a combination of the RRKM approximation and transition-state theory), one would expect all such trajectories to end up as $\text{H} + \text{O}_2$ at sufficiently low T and the vast majority to end up there even at 2500 K. However, I was not able to quantify this effect adequately at the time. Clearly it is possible for a microcanonical ensemble of HO_2^* complexes to dissociate partially to $\text{O} + \text{OH}$, particularly at the high energies that might be involved in the thermal reaction at combustion temperatures. Thus I did not distinguish between "statistical" and "non-statistical" (non-RRKM) redissociation to $\text{O} + \text{OH}$. Moreover, the Melius-Blint potential was known to be flawed, and these flaws naturally raised questions about the applicability of the results to the real physical system.

Varandas and co-workers [16, 17] subsequently addressed the same issue using their own DMBE III and DMBE IV potentials, the latter of which is still probably the best global PES available for the reaction. They confirmed the non-RRKM behavior, at least qualitatively. However, they too did not distinguish satisfactorily between "statistical" and "non-statistical" redissociation and consequently could not quantify the non-RRKM effect.

Only recently have Miller and Garrett [13] attempted to quantify the non-RRKM behavior with any degree of rigor. They used both the Melius-Blint and DMBE IV potentials; the results for the DMBE IV surface are discussed here. They also addressed the issue from two different perspectives: the effect on the thermal rate coefficient and through a direct test of the RRKM assumption itself.

First consider the effect on the thermal rate coefficient $k_{-1}(T)$. We can calculate the rate coefficient $k_c(T)$ for complex formation in the $\text{O} + \text{OH}$ reaction using μVT as

$$k_c(T) = \frac{g(T)}{hQ_R(T)} \int_0^\infty N_1(E) \exp(-E/k_B T) dE, \quad (\text{III.1})$$

where k_B is Boltzmann's constant, h is Planck's constant, Q_R is the vibrational/rotational/relative-translational partition function of the reactants, $g(T)$ is an electronic degeneracy factor, and $N_1(E)$ is the sum of states on the TSDS separating O + OH from the HO₂ well with total energy less than or equal to E . $N_1(E)/h$ may also be interpreted classically as the trajectory flux per unit energy through the TSDS. We can also calculate $k_{-1}(T)$ using μ VT and the RRKM assumption from

$$k_{-1}(T) = \frac{g(T)}{hQ_R(T)} \int_0^\infty \frac{N_1(E) N_2(E)}{N_1(E) + N_2(E)} \exp(-E/k_B T) dE. \quad (\text{III.2})$$

where $N_2(E)$ is the sum of states with energy less than or equal to E on the TSDS separating H + O₂ from the HO₂ well. Aside from the exponential, the integral in Eq. (III.2) has two factors: $N_1(E)$, which is proportional to the rate (or probability) of complex formation, and $N_2(E)/[N_1(E) + N_2(E)]$, which is the probability of reaction occurring once the complex is formed. The appearance of these two probabilities as a simple product in the integrand is an indication of their statistical independence, which in turn is a consequence of the RRKM assumption about the intramolecular dynamics of the HO₂* complex. From Eqs. (III.1) and (III.2) we can compute the RRKM probability of reaction occurring once the complex has been formed as a function of T from

$$P_{\text{RRKM}}(T) = [k_{-1}(T)/k_c(T)]_{\text{RRKM}} \quad (\text{III.3})$$

We can also compute $k_{-1}(T)$ and $k_c(T)$ using the QCT method, in which a complex is assumed to be formed any time a trajectory has at least one O - O inner turning point. Then we can define $P_{\text{QCT}}(T)$ from

$$P_{\text{QCT}}(T) = [k_{-1}(T)/k_c(T)]_{\text{QCT}}. \quad (\text{III.4})$$

The ratio $P_{\text{QCT}}(T)/P_{\text{RRKM}}(T)$ is thus a quantitative measure of the effect of non-RRKM behavior on the thermal rate coefficient (either k_{-1} or k_1).

The functions $P_{\text{QCT}}(T)$ and $P_{\text{RRKM}}(T)$ are plotted in Fig. 6 for the DMBE IV potential. Both decrease with increasing temperature. Interestingly however, the ratio $P_{\text{QCT}}/P_{\text{RRKM}} \approx 0.5$ independent of temperature all the way from 250 K to 5000 K. A similar result is found for the MB potential [13]. This result suggests that, whereas the statistical redissociation of HO₂* to O + OH is temperature dependent, the nonstatistical back dissociation does not depend on temperature at all.

Calculating the effect of non-RRKM dynamics on $k_1(T)$ necessarily involves a number of distractive issues such as identifying TSDS's, calculating sums of states, and mixing classical and quantum concepts. However, Miller and Garrett have demonstrated the effect directly using classical mechanics in the following way (thus eliminating these other issues). They computed complex-forming classical trajectories started as both O + OH and H + O₂ with the same energies and with $J = 0$. If the RRKM assumption were

satisfied, the probability of forming $O + OH$ (or $H + O_2$) should be the same for both groups of trajectories, i.e. it should be independent of origin as long as E and J are the same. Table I (DMBE IV potential), from Miller and Garrett, shows that this is not the case. There is a strong tendency for trajectories to return to the region of the potential from which they were started. Because of the mismatch between the $O - O$ and $H - O$ vibrational frequencies in the HO_2^* complex, energy does not flow freely between the $O - O$ bond and the $H - O$ bond (trajectories started as $O + OH$ initially have their energy predominantly in the $O - O$ bond and those started as $H + O_2$ have theirs predominantly in the $H - O$ bond).

The remarkably good agreement between experiment and the QCT rate coefficients on both the DMBE IV and MB potentials [13] over the very wide range of temperatures, $250\text{ K} < T < 5300\text{ K}$, argues strongly that the non-RRKM behavior described here is a real effect. However, another result casts some doubt on this conclusion. Many of the trajectories that form an HO_2^* complex and dissociate back to $O + OH$ do so with insufficient energy in the OH to satisfy the zero-point energy requirement. Of course this cannot happen quantum mechanically. There appears to be no satisfactory way of correcting the QCT results for this effect [13]. Either the non-RRKM effect is real or the uncertainty principle wipes it out. In the latter case the agreement between the trajectory results and experiment would be fortuitous, and one would be forced to conclude that both the DMBE IV and MB potentials were seriously in error. Only an exact quantum scattering calculation can resolve the issue, and such calculations have already begun to appear [18-20], but only for $J = 0$. Leforestier and Miller [18] have accounted for higher J 's using the "J-shifting" approximation. To implement this approximation it is necessary to choose a point along the reaction path at which to calculate rotational energies. The two obvious choices, the HO_2 minimum and the transition state (separating $O + OH$ from the HO_2 minimum) lead to results that correspond approximately to our QCT and RRKM results, respectively. Thus the issue is still not resolved. Reaction (R1) remains perhaps the most fascinating example of how the most detailed microscopic dynamical behavior can have a major impact on even the most macroscopic of combustion phenomena - burning velocities, extinction limits, and flammability limits.

IV. Prompt NO; The Reaction $CH(X^2\Pi) + N_2 \rightarrow HCN + N(^4S)$

The "prompt-NO" phenomenon has pervaded the combustion literature for more than 20 years [21-24]. Its underlying mechanism is an important source of NO_x in practical combustion systems, even dominant under some conditions - conventional wisdom says that "prompt NO" is the dominant source of NO_x in rich premixed combustion of all sorts and in diffusion flames [25]. However, interest in prompt NO appears to stem primarily from the controversy about its origins.

Fenimore [21] discovered prompt NO in 1971 and gave it its name. He was studying NO formation in flames fueled by hydrogen, carbon monoxide, and various

hydrocarbons at atmospheric and elevated pressures. In flames at these pressures the primary reaction zone is restricted to a very narrow, largely unresolvable region immediately adjacent to the burner. Fenimore found that his NO profiles under such conditions extrapolated to zero at the burner surface in the hydrogen and carbon monoxide flames, but the NO profiles had non-zero intercepts in all the hydrocarbon flames. Moreover, this "intercept NO," or "prompt NO," increased with increasing equivalence ratio up to $\phi \approx 1.4$. It also increased with pressure, but there was only a weak temperature dependence. Fenimore attributed the prompt NO to a reaction, in the primary reaction zones of the hydrocarbon flames, between N_2 and a hydrocarbon free radical, the products of which (presumed to involve HCN or CN) were thought to be oxidized rapidly to NO. Of course such a reaction would not occur in hydrogen or carbon-monoxide flames. Fenimore suggested two possibilities for the hydrocarbon- N_2 reaction,

apparently because they were the least offensive on energetic grounds of all the possible candidates.

A controversy arose about the origin of prompt NO, largely because reactions (R2) and (R10) seem so implausible: (R2) does not conserve electron spin and (R10) is four-centered. Hayhurst and Vince [22] discuss the controversy at length, so I shall be brief. An alternative explanation of Fenimore's observations was proposed that superequilibrium O-atom concentrations in the primary reaction zones of the hydrocarbon flames might produce the "prompt" NO through the Zel'dovich mechanism, initiated by the extremely endothermic reaction,

even though such a proposal appears to be inconsistent with Fenimore's observations about dependence of the prompt NO on temperature, pressure, equivalence ratio, and fuel type. In addition, we now know that the temperatures in the reaction zones at which such radical overshoots occur are too low to produce any significant NO through (R11) in the times available [24]. Other candidate reactions were proposed, including reactions of N_2 with C, CH_2 , and C_2H . However, all these reactions brought with them a degree of implausibility, but perhaps none more so than (R2), which was perceived to be very slow because it is "spin-forbidden."

By measuring HCN concentrations directly in rich, atmospheric-pressure, propane-air flames, Bachmeier, et al [26] established conclusively that Fenimore's prompt NO was the result of a reaction between N_2 and a hydrocarbon free radical. Blauwens, et al. [27] subsequently narrowed the candidate reactions to two,

by measuring NO and hydrocarbon free-radical concentrations in low-pressure methane, ethane, and ethylene flames. Miller and Bowman [24] have discussed the possible sources of prompt NO from a number of perspectives. They conclude that (R2) is the key reaction, with perhaps some minor contribution at very high temperature from the reaction of N₂ with carbon atoms,

It seems to be firmly established now that reaction (R2), even though it does not conserve electron spin, is the primary source of "prompt NO."

There is a paucity of experimental data on k_2 . Its direct determination has proved to be particularly elusive. Low-temperature investigations are masked by the addition reaction,

and high-temperature, shock-tube determinations are limited to $T > 2300$ K. Other values reported in the literature are indirect, largely deduced from flame experiments. A notable exception is the value given by Miller and Bowman [24] who, following Glarborg, et al. [23], deduced k_2 from modeling NO formation in the stirred-reactor experiments of Bartok, et al. [28]. These latter experiments are particularly sensitive to k_2 because they were conducted at relatively low temperatures, $T < 2000$ K, and short residence times, 2-3 msec.

An accurate theoretical description of (R2) has been just as elusive as the experimental determination of k_2 , largely because of the necessity of locating the "minimum-energy crossing point" between the doublet and quartet PES's. Miller and Walch [29] discuss at some length how the final reaction path has evolved from the efforts of a number of electronic structure theorists [30-34]. The resulting reaction path is shown in Fig. 7. It represents one of the major triumphs of electronic-structure theory in combustion.

The pressure-dependent addition reaction, detected in the low-temperature kinetics experiments [35], is a consequence of formation of the datively bonded adduct shown in Fig. 7. The temperature and pressure dependence of k_{1a} have been described accurately in the theoretical investigation of Rodgers and Smith [35] based on the PES shown here. A surprising development from the electronic-structure calculations is that this datively bonded minimum on the PES does not lie on the reaction path connecting CH (²II) + N₂ with HCN + N(⁴S) [29, 33, 34]. The latter is a completely independent reaction; its minimum-energy path is shown as the solid line in Fig. 7.

The most noteworthy feature of Fig. 7 is that the surface crossing is not the high point along the reaction path, as generally had been presumed until recently [24, 30-32]. As shown by Walch [34], the surface crossing is separated from both reactants and products by fairly high potential energy barriers. This suggests that the surface crossing itself may not play a major role in determining k_2 .

Miller and Walch [29] have taken this idea to its limit. They take the entire region of phase space bounded by the saddlepoints of the potential marked (1) and (2) in Fig. 7 as a single RRKM complex. In so doing, they implicitly assume that the relativistic spin-orbit interaction terms in the Hamiltonian that promote transitions from one surface to the other can be treated in much the same way as anharmonic vibrational mode coupling terms and vibration-rotation interaction terms are treated, i.e. they are ignored because they are so strong! In reality this approximation will be a good one as long as transitions from one surface to the other occur much more frequently than do dissociations of the complex over either of the two barriers; thus microcanonical/fixed-J equilibrium can be maintained in the complex region.

The predictions for k_2 of Miller and Walch are compared with experiment in Fig. 8. The agreement is particularly good with the direct determinations of k_2 by Dean, et al. [36] and Lindackers, et al. [37], with the Miller-Bowman result discussed above, and with the GRI-Mech expression, which should be considered to be a consensus experimental value, determined by modeling a number of flame and shock tube experiments. The good agreement of the RRKM prediction with experiment suggests that the assumption introduced by Miller and Walch may be valid, at least to a first approximation. If so, it is ironic that the factor most responsible for delaying the acceptance of "prompt NO," i.e. the non-adiabaticity of (R2), has little or no effect on the thermal rate coefficient.

V. The Thermal De-NO_x Process: NH₃ + NO → Products

The chemistry underlying the Thermal De-NO_x process has both amused and perplexed me for years. The process was developed by Richard Lyon at Exxon in the early 1970's and patented in 1975 [38, 39]. It is an after-treatment scheme commonly used on stationary combustion systems to control NO_x emissions - ammonia is the additive. The complex reaction sequence by which the ammonia removes the nitric oxide has several important properties:

- 1) The reaction requires oxygen. If there is no O₂ present, there is no NO removed.
- 2) The reaction is self-sustaining - it does not require the addition of other fuel compounds to make it go.
- 3) Nitric oxide removal is possible only in a narrow temperature range centered at $T \approx 1250$ K. At temperatures below 1100 K no reaction takes place, and at temperatures above 1400 K the ammonia is oxidized to form NO rather than destroy it.
- 4) If hydrogen (H₂) or hydrogen peroxide (H₂O₂) is added with the ammonia, the temperature window for NO removal moves to lower temperatures, but the width of the window remains unaltered.
- 5) The presence or absence of water has relatively little effect on the NO removal.

6) The reaction is not explosive. It takes place relatively smoothly in the course of approximately 0.1 sec.

Miller, Branch, and Kee [40] were the first to attempt to explain these observations in terms of elementary reactions and to propose a quantitative mathematical model for the process. Miller and Bowman [24] subsequently refined the Miller-Branch-Kee mechanism. In order to highlight the key chemical issues in the process, I review here the basic features of the Miller-Bowman model [24].

In the presence of water (i.e. in normal combustion products) ammonia is converted to NH_2 by reaction with hydroxyl,

Consequently, the process must produce OH as a by-product or the reaction would very quickly die out. It has been obvious from the beginning that the reaction between NH_2 and NO is key. This reaction must simultaneously remove NO and produce free radicals. It is now well established [41] that this reaction has two channels,

Also, the radical channel must constitute at least 25% of the total reaction. This is because a hydrogen atom formed either directly or indirectly from NNH leads to three OH's in the presence of oxygen, i.e.

Thus k_{3a} cannot be more than three times as large as k_{3b} or the reaction would die out.

The process is limited at high temperatures by the chain-branching sequence occurring too rapidly, thus producing hydroxyl concentrations that are so large that the reaction of NH_2 with OH is able to compete with the $\text{NH}_2 + \text{NO}$ reaction. The following sequence then takes place:

This sequence produces NO. Therefore, at temperatures greater than $T \approx 1400 \text{ K}$ there is a net increase in the nitric oxide.

The requirement that the reaction not be explosive forces the chain carrier growth to be self-limiting. This constraint is related to the dependence of the NO removal on H_2 addition, water concentration, and O_2 level [24, 39, 41], i.e. when the reaction is explosive, these other effects are not predicted accurately by the model. When NNH dissociates rapidly, i.e.

chain-carrier growth is inevitably explosive. In the Miller-Bowman/Miller-Branch-Kee model the dominant NNH reaction is

As the reaction proceeds in time, the HNO initially dissociates and produces the branched-chain sequence. However, the hydroxyl concentration eventually reaches a point where the chain-terminating reaction,

is able to compete with HNO dissociation. Thus the branched-chain sequence is self-limiting, i.e. the faster the chain branching occurs, the sooner the chain termination step comes into play to slow it down. The requirement from modeling that NNH live long enough to react with NO places a lower limit on the NNH lifetime - according to Glarborg, et al. [42], this limit is about 10^{-6} sec.

From the foregoing discussion, largely borrowed from Miller and Glarborg [41] and Miller and Bowman [24], it is clear that two kinetic parameters are critical to the quantitative description of Thermal De- NO_x : the branching fraction $\alpha = k_{3b}/(k_{3a} + k_{3b})$, of the $\text{NH}_2 + \text{NO}$ reaction and the lifetime of NNH, $\tau_{\text{NNH}} = 1/k_{21}$. The interplay between theory and modeling has played a major role in determining these parameters, and thus in developing the reaction mechanism as we currently understand it. In the remainder of this section I focus on these issues.

To understand the Thermal De- NO_x mechanism it is essential to understand the $\text{NH}_2 + \text{NO}$ reaction. The seminal contribution to this subject came from the BAC-MP4 electronic structure calculations of Melius and Binkley [43]. Subsequent calculations by different methods have produced only minor quantitative differences from their original work - the essential features remain the same. Figure 9 is a reaction coordinate diagram from the most recent calculations of Durant and co-workers [44]. It defines clearly the sequence of internal rearrangements required for the initial NH_2NO adduct to produce $\text{N}_2 + \text{H}_2\text{O}$ (the dominant channel) with no intrinsic energy barrier, and it shows the existence of a slightly endothermic radical channel, $\text{NNH} + \text{OH}$, which can occur through the dissociation of any of several intermediate adducts.

One of the most commonly asked questions about the $\text{NH}_2 + \text{NO}$ reaction concerns the possibility of stabilizing (by collision) one or more of the intermediate complexes. This question is easily answered from rudimentary knowledge of the stationary points on the PES, i.e. structure and normal-mode analysis. From this information and the harmonic-oscillator, rigid-rotor approximation, one can calculate $k(E)$,

$$k(E) = \frac{1}{h} \frac{N^+(E)}{\rho(E)}, \quad (\text{V.1})$$

where $N^+(E)$ is the sum of states with energy less than or equal to E for a TSDS placed at an appropriate saddlepoint, and $\rho(E)$ is the density of states per unit energy for the adduct in question. From $k(E)$, one can calculate $\tau(E) = 1/k(E)$, the lifetime of the complex at

energy E. Lifetimes for the various adducts to isomerize further along the reaction path are given in Fig. 9 for the PES of Wolf, et al. [44]. Results for two different energies are given: $E = 0$, the minimum energy from which a complex can be formed from $\text{NH}_2 + \text{NO}$, and the energy corresponding to the peak of a thermal distribution at $T = 1100 \text{ K}$ above this point ($T = 1100 \text{ K}$ corresponds to a typical Thermal De- NO_x temperature). One can compare these lifetimes with the mean times between collisions τ_c at various temperatures and pressures, e.g. $\tau_c = 3.4 \times 10^{-10} \text{ sec.}$ at $T = 1100 \text{ K}$ and $p = 1 \text{ atm.}$ These results show without question that stabilization of any of the intermediate complexes under Thermal De- NO_x conditions is an unlikely event, at least for pressures up to about 5 to 10 atm., i.e. none of the complexes live long enough to undergo a collision. This conclusion is consistent with a similar analysis performed by Phillips [45] using a different PES, which indicated that complex lifetimes were $\sim 10^{-11} \text{ sec.}$ These calculations explain the experimental observation that $k_3 = k_{3a} + k_{3b}$ is independent of pressure from a few Torr up to almost an atmosphere [46] at room temperature. It is quite remarkable that reaction (R3a), which requires the breaking of all three bonds in the reactants and the formation of three completely new bonds, takes place as a very fast ($k_{3a} \approx 1 \times 10^{13} \text{ cm}^3/\text{mole-sec}$ at 300 K) elementary step under normal conditions.

The NNH radical is a strange entity in combustion chemistry, and its lifetime is a critical feature of a successful Thermal De- NO_x kinetic model. Figure 10 shows a reaction-coordinate diagram for NNH dissociation drawn from the PES calculations of Walch and co-workers [47]. The hydrogen atom is bonded precariously to the N_2 molecule, and dissociation to $\text{N}_2 + \text{H}$ occurs exothermically (without requiring collisions) by tunneling through the barrier shown in the diagram. This makes the lifetime very short. How short? Well, the earliest theoretical estimate was $\tau_{\text{NNH}} \approx 10^{-11} \text{ sec.}$, much smaller than the Miller-Bowman value of $\tau_{\text{NNH}} = 10^{-4} \text{ sec.}$ (which was inferred from room temperature experiments on the products of the $\text{NH}_2 + \text{NO}$ reaction [24]) and the Glarborg, et al lower limit of $\tau_{\text{NNH}} = 10^{-6} \text{ sec}$ (required to avoid unconstrained explosive behavior in Thermal De- NO_x modeling by allowing (R22), $\text{NNH} + \text{NO} \leftrightarrow \text{N}_2 + \text{HNO}$, to compete with NNH dissociation). However, the best theoretical prediction is due to Koizumi, et al [48], who calculated a lifetime of τ_{NNH} between 10^{-9} and 10^{-8} sec. from a complete coupled-channel quantum scattering calculation on the PES of Walch, et al. [47] - still smaller than 10^{-6} sec.

Experimentally, the only attempt at a direct determination of τ_{NNH} is that due to Selgren, et al. [49]. They deduced $\tau_{\text{NNH}} \leq 0.5 \text{ } \mu\text{sec.}$ Even though their result may be influenced somewhat by the presence of excited electronic states of NNH, it seems likely that τ_{NNH} is smaller than the lower limit deduced by Glarborg, et al. However, it is not clear how much smaller it is. The theoretical predictions are very sensitive to small uncertainties in PES parameters, such as the barrier height and exothermicity of Fig. 10, used in the tunneling calculations.

The only way that the Miller-Bowman mechanism can accommodate $\tau_{\text{NNH}} < 10^{-6}$ sec. is if NNH reacts with something more abundant than NO, and molecular oxygen is the only real possibility,

However, as discussed by Miller, Branch, and Kee [40] and Miller and Bowman [24] the formation of HO_2 leads to the conversion of the NO to NO_2 ,

in conflict with experimental observations that no NO_2 is produced in the Thermal De- NO_x process under normal operating conditions. This observation has placed a very strict upper limit on the values k_{24} can have in the Miller-Bowman model, even though at first glance one would expect (R24) to be very fast - it involves the extremely exothermic (~ 60 kcal/mole) abstraction of a tenuously held hydrogen atom.

There appears to be only one way out of this dilemma. In the model one can allow a small value of τ_{NNH} and a fast (R25) only if the NO_2 produced in (R25) is converted rapidly back to NO. Then the NO_2 would be transparent to experimental observation. BAC-MP4 calculations [51] indeed show that the reaction between NH_2 and NO_2 has two exothermic channels,

neither of which has an intrinsic energy barrier. Reaction (R26a) is completely analogous to (R3a), and (R26b) involves the attack of NH_2 on one of the O atoms of NO_2 , followed by N-O bond fission. Early experiments on (R26) [50] indicated that the reaction produced $\text{N}_2\text{O} + \text{H}_2\text{O}$ almost exclusively at room temperature, but there was no information on the products at higher temperatures until very recently.

This situation prompted Glarborg, et al. [51] to study the reaction between NH_3 and NO_2 in a flow reactor at temperatures applicable to Thermal De- NO_x , $850 \text{ K} < T < 1350 \text{ K}$. Indeed they found that NO was the primary product of the reaction and that N_2O was only a minor by-product. They were able to explain quantitatively their results with a simple branched-chain mechanism in which (R26b) was the key step. They deduced $k_{26b} \approx 3.5 \times 10^{12} \text{ cm}^3/\text{mole-sec}$ assuming that lower-temperature data on the total rate coefficient was applicable to (R26a) and extrapolatable to the temperatures of interest. However, recent experiments [52-53] indicate that (R26b) may be the dominant channel even at lower temperatures. These newer experiments are in excellent agreement with the results of Glarborg, et al. in the overlapping temperature range, $850 \text{ K} < T < 990 \text{ K}$.

This new information has allowed Miller and Glarborg [41] to construct a new kinetic model for the Thermal De- NO_x process. They did so by comparing model predictions with the experimental results of Kasuya, et al. [54], who measured not only the NO removed, but also the NO_2 and N_2O formed in Thermal De- NO_x experiments over a wide range of initial O_2 levels, 0.1% to 50%. The temperature at which NO removal

begins to take place for any initial oxygen concentration is extremely sensitive to the competition between NNH dissociation and reaction (R24), $\text{NNH} + \text{O}_2 \leftrightarrow \text{N}_2 + \text{HO}_2$. By modeling these initiation temperatures as a function of oxygen concentration, with the assumption that (R24) was very fast ($k_{24} = 2 \times 10^{14} \text{ cm}^3/\text{mole-sec.}$), they deduced $\tau_{\text{NNH}} = 10^{-7} \text{ sec.}$ This value is still larger than the best theoretical prediction, but it is now less than the upper limit set by the experiments of Selgren, et al. Moreover, the Miller-Glarborg mechanism predicts well the experimental NO_2 and N_2O concentrations over the entire range of initial O_2 levels. At high O_2 concentrations the N_2O is formed primarily by (R26a), $\text{NH}_2 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$, i.e. from NO_2 , whereas at low O_2 concentrations the N_2O comes principally from $\text{NH} + \text{NO} \leftrightarrow \text{N}_2\text{O} + \text{H}$. The prediction by the model of the complex T and O_2 dependence of the N_2O produced is strong support for the basic structure of the model. The Miller-Glarborg mechanism is shown diagrammatically in Fig. 11.

If one restricts τ_{NNH} to small values, say $\tau_{\text{NNH}} \leq 0.5 \text{ } \mu\text{sec}$ as indicated above, the initiation temperatures for low O_2 levels do not depend on (R24), i.e. the NNH always dissociates! Consequently, under these conditions the initiation temperatures depend only on the branching fraction α of reaction (R3). Miller and Glarborg used the functional form,

$$\alpha(T) = AT^n, \quad (\text{V.2})$$

and determined A and n from the known room temperature value of α and the value they inferred from modeling the initiation temperature at an initial O_2 concentration of 0.1% in the Kasuya experiments. This result ($n = 0.9$) is compared in Fig. 12 with the "direct" determinations of α , most of which were obtained at temperatures lower than those of interest for Thermal De- NO_x . Also shown in the figure are various $\alpha(T)$ functions for different values of the parameter n in Eq. (V.2). It should be noted that this functional form was motivated by my prior experience with the $\text{NH} + \text{NO}$ reaction, where it describes very accurately the theoretical results for the minor $\text{N}_2 + \text{OH}$ channel [55]. However, there is no a priori reason to expect it to work here. Nevertheless, it has been a point of consternation that virtually all the direct measurements of $\alpha(T)$ lie even below the $n = 0.7$ curve, which was shown by Glarborg, et al. [42] to be the minimum value of n for which NO removal could occur for reaction times, temperatures, and initial compositions of interest, even with an infinitely fast NNH dissociation.

Glarborg and Miller [56] have used the observation that, at very low O_2 levels, initiation temperatures for NO removal are determined completely by α to extract values of α from Thermal De- NO_x experiments performed for a variety of initial compositions and pressures. These results are also plotted in Fig. 12. It is intriguing that these results appear to blend smoothly with the most recent direct measurements of Park and Lin [57]. However, if this consistency is real the temperature dependence of $\alpha(T)$ must be more complicated than that given by Eq. (V.2). Further evidence that a sharp rise in $\alpha(T)$ may occur somewhere between $T = 1000 \text{ K}$ and $T = 1200 \text{ K}$ is provided by the recent modeling

of static cell experiments by Halbgewachs, et al. [58] and from previous flow reactor [59] and NH_3 - NO flame [60-61] experiments.

Clearly, the missing element in the puzzle is an accurate theoretical description of the (statistical) dynamics of the $\text{NH}_2 + \text{NO}$ reaction, one that can tell us what to expect from what we know about the PES and how modifications of the PES might affect $\alpha(T)$. Diau and Smith [61] have recently provided such a theoretical treatment. They model the various rearrangements shown in Fig. 9 with a set of stochastic differential equations, the transition probabilities $k(E, J)$ in which are calculated from RRKM theory (such a theoretical treatment was first given for a different reaction by Miller, Parrish, and Brown [63]). Appropriate thermal averaging results in expressions for $k_{3a}(T)$ and $k_{3b}(T)$. Two features of their analysis are key to making accurate predictions:

- 1) a variational ($\mu\text{VT-J}$) treatment of the bond-forming ($\text{NH}_2\text{-NO}$) and bond-breaking (NNH-OH) steps
- 2) angular momentum conservation through all the possible transitions.

A rigorous handling of angular momentum conservation is essential in this reaction. The branching fraction $\alpha(T)$ is governed primarily by the competition between the trans-cis isomerization steps shown in Fig. 9,

and the NNH-OH bond fission steps. The former have tight transition states whose centrifugal barriers grow rapidly with increasing J , whereas the latter have loose transition states whose centrifugal barriers do not increase significantly with J . Thus there is the possibility that high temperatures (high J 's) could effectively shut off the $\text{N}_2 + \text{H}_2\text{O}$ channel, the phenomenon known as rotational channel switching [64, 65]. Such an effect must be contained within any satisfactory theoretical treatment of reaction (R3).

Because of the lack of sufficient information about the bonding reaction paths (NH_2 - NO and $\text{NNH} - \text{OH}$) from electronic structure calculations, Diau and Smith were forced to make the standard Wardlaw-Marcus [66] assumptions about these portions of the PES, one of which is to use a Morse function to describe the potential along such reaction coordinates. Diau and Smith adjusted the β 's in the Morse functions to predict correctly the known room-temperature values of k_3 and α . With just these two adjustable parameters and Walch's [67] thermochemistry and saddlepoint properties, they predicted accurately the temperature dependence of $k_3(T)$ and the $\alpha(T)$ shown in Fig. 12. Indeed, their results indicate clearly that a rapid rise in $\alpha(T)$ with temperature is to be expected from our present knowledge of the PES. Moreover, Diau and Smith show that their predictions are relatively insensitive to their choice of β 's and, not surprisingly, depend most strongly on the endothermicity (or exothermicity) of the radical channel. Although their current

predictions do not show a sharp rise in $\alpha(T)$ at $T \approx 1000$ K, it is quite possible that such a feature may arise when more accurate PES information becomes available.

The Thermal De-NO_x process involves an unusually large amount of subtle chemical behavior, so much so that it might be used to encapsulate the potential impact that the vast apparatus of theoretical chemistry can have on combustion. Probably in no other application have careful modeling of laboratory experiments and theory combined so coherently to enhance our knowledge of a combustion process.

VI. The Formation of Aromatic Compounds in Flames of Aliphatic Fuels: $C_3H_3 + C_3H_3 \rightarrow$ Products and the importance of resonantly stabilized free radicals

Perhaps the most challenging problem in combustion chemistry is the quantitative prediction (and its associated understanding) of concentrations of aromatic compounds, polycyclic aromatic compounds (PAH), and their precursors in flames burning aliphatic fuels. This topic has long been of interest because of its connection with soot formation, but interest in it has increased since the Clean Air Act Amendments of 1990 regulated the emissions of many such compounds from industrial burners, calling them "air toxic species." The accurate modeling of such species in flames requires dealing with a degree of complexity not encountered in the problems discussed so far in this paper. Consequently, many of the important issues are only beginning to take focus, and few have been resolved satisfactorily.

The seminal work in this area is due to Frenklach and co-workers [68-71], who dealt primarily with acetylene pyrolysis and combustion. They developed what now might be called the "standard model" for ring formation and PAH growth. In the standard model ring formation occurs by the reaction between a C₄-hydrocarbon and a C₂-hydrocarbon. The main channels are

where C₆H₅ is phenyl and C₆H₆ is benzene. Larger polycyclic aromatics are formed from smaller ones by a sequence of steps involving hydrogen abstraction, acetylene addition, and cyclization. The standard model has been extremely important for two reasons: it provides a clear conceptual picture of how PAH and soot might form in flames of aliphatic fuels, and it has provided a basic structure on which subsequent research has built. However, many details of the model now have been called into question.

A number of investigators [72-77] independently have suggested that the reaction between two propargyl radicals,

might be a key cyclization step in flames. Moreover, Miller and Melius [72] showed that reactions (R27) and (R28) could not account for benzene levels observed in lightly sooting, low-pressure acetylene flames, largely because $n\text{-C}_4\text{H}_3$ and $n\text{-C}_4\text{H}_5$ are relatively easily converted to the more stable *i*-isomers. They also calculated, using the BAC-MP4 method, several low-energy reaction paths with no intrinsic energy barriers leading from $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ to benzene (or phenyl + H), consistent with observations that (R29) is very fast [76, 78]. Miller and Melius also emphasized the potential importance of resonantly stabilized free radicals (RSFR) such as propargyl in forming aromatics and PAH in flames.

Figure 13 shows the electronic structures of several resonantly stabilized free radicals potentially important in the formation of small (one or two rings) aromatic compounds in flames of C_1 and C_2 hydrocarbon fuels. For such radicals the unpaired electron is delocalized in the molecule, resulting in at least two resonant electronic structures of comparable importance. As a result of the delocalization of the unpaired electron, such radicals generally form weaker bonds than do normal radicals, particularly with stable molecules (including O_2). The addition complexes formed in the latter case thus do not readily support rearrangement, making the radicals relatively unreactive. Consequently, such free radicals can attain high concentrations in flames, making them attractive as building blocks of higher hydrocarbons, particularly if the higher hydrocarbons can be formed by reaction of one resonantly stabilized free radical with another.

Based on the work of Miller and Melius on acetylene flames and the recent work of Marinov and co-workers [79, 80] on CH_4 , C_2H_6 , and C_2H_4 flames, the consistent picture is emerging that reaction (R29) and analogous reactions involving radical-substituted propargyls (RCCCH_2) are responsible almost exclusively for the formation of the first aromatics in these flames. The most important reaction other than (R29) is

where the benzyl produced in (R30) forms toluene by H addition. Similarly, ortho-xylene can be formed from the combination of two 1-methylallenyl radicals. It should not go unnoticed that the R in RCCCH_2 could be a large PAH radical, in which case reactions such as

could play a role in PAH growth. All these reactions involve two RSFR's as reactants.

Reactions between two RSFR's have also been suggested as possible sources of naphthalene $\langle \text{萘} \rangle$ in flames [81, 82]

Melius, et al [81] have shown how (R31) might take place, although a fairly large intrinsic energy barrier is involved. Reaction (R32) also looks attractive, but drawing any conclusion about naphthalene formation in flames is premature at this point.

Except for acetylene flames, in which C_3H_3 is formed by the sequence,

RSFR's are intimately involved in forming the C_3H_3 and CH_3CCCH_2 that lead to cyclization in the C_1 and C_2 hydrocarbon flames. In methane and ethane flames the key radical is alkyl (C_3H_5), which is formed by the reaction,

Successive hydrogen abstractions from allyl lead to propargyl,

where C_3H_4 is allene. Cyclization then occurs through (R29), or propargyl can react with methyl,

and cyclization can occur through (R30). The latter sequence is more likely in methane than in ethane flames.

In ethylene flames the key RSFR is $i-C_4H_5$, which is formed by

and by the sequence,

The $i-C_4H_5$ radical can then react with H atoms to produce either propargyl or 1-methylallenyl;

Cyclization then occurs through (R29), (R30), or the combination of two CH_3CCCH_2 radicals.

Clearly the reaction between two propargyl radicals plays a key role in the formation of aromatic compounds in current flame models. Therefore it is essential that we understand how this reaction takes place. Its theoretical analysis introduces some complications not heretofore considered. These complications arise primarily because of

the larger number of atoms (higher dimensional phase space) in the $C_6H_6^*$ complexes formed than in those of the reactions discussed in the earlier sections of the paper.

Figure 14 is a reaction coordinate diagram for reaction (R29) based on the BAC-MP4 electronic structure calculations of Miller and Melius [71] and Melius, et al. [83]. Various aspects of the reaction have been discussed previously [83]. The point I wish to consider here is the possibility of stabilizing one of the intermediate complexes as an alternative to the products ($C_6H_5 + H$ or benzene) written by Miller and Melius. A definitive discussion of this issue requires the solution of a "multiple-well" master equation that includes both isomerization and association/dissociation terms as well as those for collisional energy transfer [65]. Such an analysis for a much simpler system has already been performed by Bedanov, et al. [84]. However, some very simple considerations can be illuminating in the present case.

Table II contains lifetimes for the various complexes shown in Fig. 14 to isomerize to the next complex along the reaction path at three different energies ($E = 0, 20$, and 50 kcal/mole) above the $C_3H_3 + C_3H_3$ asymptote. These energies correspond to peaks of thermal distributions in adduct I (1,5-hexadiyne) at temperatures of 0 K, 1000 K, and 1500 K respectively, and thus they correspond roughly to energies one might expect to have from $C_3H_3 + C_3H_3$ "chemical activation" at these temperatures. Also shown in the table are values of τ_c at 1 atm and at 25 Torr, a pressure typical of low-pressure flame experiments. The third set of entries in the table is for f_b ,

$$f_b = 1/Q \int_0^{E_b} \rho(E) \exp(-E/k_B T) dE, \quad (VI.1)$$

where Q is the vibrational-rotational partition function,

$$Q = \int_0^\infty \rho(E) \exp(-E/k_B T) dE, \quad (VI.2)$$

and E_b is the potential energy barrier to isomerization. Thus f_b is the fraction of molecules in a thermal distribution at temperature T that are stable to isomerization. The remainder $1 - f_b$ are free to isomerize and ultimately will do so even in a collision-dominated environment. Remember that the ultimate product of collisions is a thermal distribution. If a large portion of this distribution lies above the isomerization barrier, one may assume that these complexes will "spill over" into other parts of the potential, at least well away from chemical equilibrium (at which they would be replaced by complexes going in the other direction).

Examination of Table II reveals that in most cases the complexes live long enough to suffer several collisions, even in a 25 Torr flame, but the thermalized adducts in a flame, where the reaction-zone temperature normally is between 1500 K and 2000 K, are unstable to isomerization. The most noteworthy exception is fulvene (adduct IV) which, at $E=50$ kcal/mole, $T = 1500$ K, lives long enough to suffer about 20 collisions and whose thermal

distribution is 91% stable to isomerization to benzene. Somewhat surprisingly, 2-ethynyl-1,3-butadiene (adduct VI) also appears feasible as a stabilization product, at least at $T = 1500$ K.

Even though adducts IV and VI live long enough to suffer multiple collisions and have stable thermal distributions under flame conditions, deactivating these complexes requires removal of large amounts of energy, and consequently a large number of collisions. It may happen that the vast majority of these complexes ultimately isomerize after suffering many collisions. Only a master-equation analysis can provide this information.

There is an intriguing phenomenon that arises when we consider isomerizations of molecules as large as these. Lifetimes for states at energies significantly above an isomerization barrier can become exceedingly long, so long that the isomerization will not take place in any time of interest. In such cases the molecule becomes "dynamically trapped", too much time being required for the molecule to accumulate enough energy in the right degree of freedom for reaction to take place. Consider a concrete example. At an energy 5 kcal/mole above its isomerization barrier, adduct V (1, 2 hexadiene-5-yne) has a lifetime of 2.4×10^{-3} sec. Such an energy has significant population in thermal distributions at temperatures in the 1000 K to 1500 K range, and this lifetime is approximately three times as large as τ_p , the mean time that the gases spend in the reaction zone of an atmospheric-pressure laminar flame! Therefore, there must exist conditions, perhaps more dramatic for larger molecules, at which molecules are thermodynamically unstable (in the sense described above) but dynamically trapped. How such conditions manifest themselves in terms of rate coefficients and product distributions is not clear.

One can draw two conclusions from these simple considerations:

1) Adducts I and II are not very likely to be stabilized in flames at pressures up to 1 atm. Their lifetimes appear to be too short, and they are thermodynamically unstable at flame temperatures. The situation concerning III and V is unclear.

2) Fulvene, 2-ethynyl-1,3-butadiene, and benzene appear clearly to be possible stabilization products formed from $C_3H_3 + C_3H_3$ under flame conditions, but a definitive conclusion on this point requires a more sophisticated, master-equation analysis, one that should be pursued in the near future. The question of whether benzene can be stabilized before it dissociates to phenyl + H is particularly tricky, because it requires information about the loose reaction path separating benzene from the dissociation products. This loose reaction path may result in lifetimes for benzene complexes that are shorter than those for fulvene, potentially making benzene less likely as a stabilization product than fulvene.

Concluding Remarks

Combustion chemistry is a complex and fascinating subject. Its successful practitioners must deal with a wide variety of *macroscopic phenomena* from a *microscopic*

perspective. In this paper I have chosen four examples to illustrate this point. They are not the only ones. However, the power of theoretical chemistry is only beginning to be felt in combustion. The first ten years or so of the next century should see an explosion of knowledge and predictive power that most of us never dreamed would occur.

Acknowledgments

I would like to thank Charlie Westbrook and Norbert Peters for inviting me to write this paper and to give the accompanying lecture. I would also like to thank Peter Glarborg, Mary Bui-Pham, Joe Durant, Steve Walch, Bruce Garrett, Nick Marinov, and Connie Miller for their help in preparing the paper. Most importantly, I want to acknowledge the fruitful collaborations that I have had for many years with my colleagues Bob Kee and Carl Melius. Their influence on my thinking pervades the entire paper. This work was supported by the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

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Figure and Table Captions

Figures

1. Schematic diagram showing various ways in which a classical trajectory may cross a transition-state dividing surface. The diamonds mark crossings in the Reactants (R) $\rightarrow$ Products (P) direction.
2. Schematic diagram illustrating the RRKM assumption. The diagram shows different excitations in phase space of an energized molecule at a specific E and J. Before any significant reaction can take place, i.e. for $t \ll \tau_R$, where τ_R is the characteristic reaction time, each ensemble evolves to fill the phase space available to it. Reaction thus always takes place from a microcanonical/fixed-J ensemble.
3. Sensitivity diagram for burning velocities of methane-air mixtures at atmospheric pressure. The sensitivity coefficient is

$$S_i = \frac{A_i}{V_u} \frac{\partial V_u}{\partial A_i}$$
 where V_u is the burning velocity and A_i is a temperature-independent factor in the i^{th} rate coefficient.
4. Temperatures in methanol/carbon-monoxide/O₂ flames (11 atm), diluted in CO₂, at which the peak rates of the indicated reactions occur as a function of oxygen mole fraction. The intersection of the curves can be identified as the flammability limit.
5. Reaction coordinate diagram for reaction (R1), $\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}$.
6. Probability that an HO₂* complex, formed from O + OH, will dissociate to H + O₂ on the DMBE IV potential. The points are trajectory results, and the lower solid curve is the least squares fit to the trajectory results ($P_{\text{OCT}}(T) = 2.56 T^{-0.248} \exp(-52.3/T)$). The upper solid line is the RRKM prediction using the μVT result

for $N_1(E)$ and the dashed line uses a trajectory result for $N_1(E)$ (the differences between the two cases are inconsequential for the present purposes).

7. Reaction coordinate diagram for reaction (R2), $CH + N_2 \leftrightarrow HCN + N$. The solid line shows the reaction path for (R2), and the dashed line shows the datively bonded adduct responsible for reaction (R2a), $CH + N_2 (+M) \rightarrow HCN_2(+M)$, and the high potential energy barrier separating it from the minimum-energy crossing point between the doublet and quartet surfaces.
8. Arrhenius plot comparing the Miller-Walch [29] prediction of k_2 , $k_2 = 3.68 \times 10^7 T^{1.42} \exp(-20723/RT)$ cm³/mole-sec for $1000 \text{ K} < T < 4000 \text{ K}$, with a variety of experimental results.
9. Reaction coordinate diagram for reaction (R3), $NH_2 + NO \rightarrow$ products. The numbers under the stable minima are RRKM lifetimes (sec.) for isomerizations "to the right." The first number corresponds to the minimum energy from which the complex can be formed from $NH_2 + NO$; the second number corresponds to the energy at the peak of a thermal distribution at $T = 1100 \text{ K}$ above this minimum. The lifetimes for II are for $II \rightarrow IV$ transitions, whereas the $II \rightarrow III \rightarrow V$ route may be faster. Also inset are mean times between collisions, τ_c , for three temperatures.
10. Reaction coordinate diagram for NNH dissociation.
11. Reaction path diagram for the Miller-Glarborg mechanism for Thermal De- NO_x . The chain branching comes from NNH dissociation, HNO dissociation, and from H_2NO dissociation. The self-limiting property of the branched chain sequence comes primarily from $OH + HNO \leftrightarrow NO + H_2O$, as in the Miller-Bowman mechanism.
12. Branching fraction $\alpha(T) = k_{3b}/(k_{3a} + k_{3b})$ as a function of temperature. The curves labeled by a value of n are described in the text. The points are direct experimental determinations and the unpublished results of Glarborg and Miller, obtained from modeling Thermal De- NO_x experiments at low oxygen levels.
13. Electronic structures of some resonantly stabilized free radicals.
14. Reaction coordinate diagram for $C_3H_3 + C_3H_3 \rightarrow$ products. (a) products formed from head-to-head or tail-to-tail recombination. (b) most important products accessible via head-to-tail recombination. Note that both reaction paths lead to fulvene and on to benzene and phenyl + H.

Tables

- I. No caption
- II. Isomerization lifetimes, τ_c , and f_b at various temperatures and pressures. The roman numerals refer to the stable minima shown in Fig. 14. The numbers in parentheses are the isomerization lifetimes in units of τ_c at 1 atm and 1500 K. Because the lifetime for $II \rightarrow III$ isomerization is so short, $II + III$ has been considered to be a composite species. The isomerization lifetime for $(II + III) \rightarrow IV$ has been calculated taking into account both the intervening transition states.

NON-RRKM EFFECT (J=0)
Varandas' DMBE IV Potential

Total Energy (kcal/mole)	Fraction of complexes that dissociate to O + OH	
	From O + OH	From H + O ₂
0-1	0.431	0.036
1-2		
2-3	0.420	0.061
3-4		
4-5		
5-6	0.579	0.189
.		
10-11	0.541	0.136
.		
15-16	0.732	0.253
.		
20-21	0.729	0.229
.		
50-51	0.786	0.289

Table I

TABLE II

<u>Adduct</u>	Lifetime (sec.) at E (kcal/mole)		
	E = 0	E = 20	E = 50
I (→ II)	3.5×10^{-9} (10.9)	4.9×10^{-10} (1.5)	8.8×10^{-11} (0.3)
II (→ III)	3.7×10^{-10} (1.2)	1.1×10^{-10} (0.3)	3.4×10^{-11} (0.1)
II & III (→ IV)	2.0×10^{-7} (625)	2.4×10^{-8} (75)	3.8×10^{-9} (11.9)
IV (→ Benzene)	6.9×10^{-5} (2.2×10^5)	3.5×10^{-6} (1.1×10^4)	1.9×10^{-7} (594)
V (→ VI)	8.6×10^{-7} (2.7×10^3)	5.1×10^{-8} (159)	5.1×10^{-9} (15.9)
VI (→ IV)	4.4×10^{-4} (1.4×10^6)	4.7×10^{-6} (1.5×10^4)	1.1×10^{-7} (344)

Mean Time Between Collisions, τ_c (sec)			
T =	1000 K	1500 K	2000 K
P			
1 atm	2.61×10^{-10}	3.20×10^{-10}	3.69×10^{-10}
25 Torr	7.93×10^{-9}	9.73×10^{-9}	1.12×10^{-8}

Adduct	Fraction of Thermal Distribution Below Isomerization Barrier		
	1000 K	1500 K	2000 K
I.	0.44	0.02	.0006
II.	0.25	0.07	0.0001
III.	0.96	0.36	0.04
IV.	1.00	0.91	0.41
V.	0.69	0.07	0.003
VI.	1.00	0.66	0.14

Fig. 1

Fig. 2

Sensitivity for Methane/Air Flames

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

NH₂+NO branching fraction

Fig. 12

Propargyl (C_3H_3)

Allyl (C_3H_5)

i - C_4H_5

i - C_4H_3

1 - methyl allenyl (CH_3CCCH_2)

Cyclo-pentadienyl ($c-C_5H_5$)

Benzyl ($C_6H_5CH_2$)

Fig. 14a

Fig. 14b