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FUNDAMENTAL AND SEMI-GLOBAL KINETIC
MECHANISMS OF HYDROCARBON COMBUSTION

Progress Report, March 1–September 30, 1977

By
Irvin Glassman
Frederick L. Dryer

MASTER

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Department of Aerospace and Mechanical Sciences
Princeton University
Princeton, New Jersey

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for Period March 1 - September 30, 1977

Irvin Glassman and Frederick L. Dryer
Principal Investigators

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Abstract

Major emphasis in combustion research is being given to the study of oxidation of hydrocarbon fuels to lend insight into the modelling of combustion processes. The introduction of combustion chemistry into the already complex turbulent flow situations which exist in practical devices make modelling exceptionally difficult. Semi-global reaction mechanisms offer the potential of reducing the overall chemical kinetic complexity, thus substantially reducing the computational barriers to appropriate modelling of combustion processes.

Reported here are the results of efforts presently underway at Princeton under ERDA support, to provide a general understanding of hydrocarbon oxidation. Specifically the results of studies of the lean oxidation of ethane along with the developed semi-global rates are reported. Initial results for the lean oxidation of propane are discussed and the present status of studies on methanol oxidation is also reported.

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I. Introduction

Major emphasis in combustion research is being given to the study of oxidation of hydrocarbon fuels to lend insight into the modelling of combustion processes. The introduction of combustion chemistry into the already complex turbulent flow situations which exist in practical devices makes modelling exceptionally difficult. Semi-global reaction mechanisms offer the potential of reducing the overall chemical kinetic complexity, thus substantially reducing the computational barriers to appropriate modelling of combustion processes.

Although the detailed oxidation chemistry of carbon monoxide, hydrogen and methane is understood, present understanding of the high temperature pyrolysis and oxidation of more realistic and alternate fuels is limited. The objective of the present program is to provide an understanding of the oxidation of more complex hydrocarbons than methane. Present work has concentrated on ethane and propane oxidation, although hydrocarbon species as complex as octane are to be studied. In addition, a study of the oxidation of methanol, potentially an important alternate fuel, has been undertaken. Global and/or semi-global techniques are being utilized to model the results of this work.

This progress report will detail the understanding gained to date and outline the progress likely to be made between now and the end of the current funding period, September 30, 1977. Since the present program was initiated recently (March 1, 1977) only modest progress has been made on the overall combustion problems alluded to above. Nonetheless, important insights have been gained already which bodes well for the success of the entire program.

II. Research Approach, Status and Results

A. Turbulent Flow Reactor

The experimental studies are presently being carried out in a newly completed arc plasma heated turbulent flow reactor. A direct liquid-gas conversion system is the source of nitrogen carrier gas. Possible contaminants from anode/cathode erosion in the plasma jet have been controlled through a composite material design derived during the custom construction of the jet (TAFA division of Humphey's Corp., Bow, N. H.). Ions are eliminated in a recombination/mixing plenum far upstream of the reactor. Available instantaneous heating characteristics accommodate rapid run preparation and maximum system temperatures to greater than 1500 K. A resistance heated inlet section mounted between the arc plasma generator and the reactor assembly has been designed to independently accommodate addition of up to two (thermally stable) reactant species as well as prevaporized water. This section is also necessary to produce uniform turbulent flow prior to the reactor assembly. Inlet temperature to the assembly is monitored in this section with thermocouple instrumentation.

The main reactor tube is of fused silica ten centimeters in diameter and approximately 185 cm in length including a 28 cm nozzle inlet mixing section. Fused-silica walls further assure elimination of surface reaction effects. There are two additional reactor tube inserts available to reduce the test section diameter to 7.0 and 5.0 cm. Thus the reactor residence time range can be significantly shortened (factor of 4) and reactor surface-to-volume ratio increased (factor of 2). The reactor mixing inlet can accommodate independently controlled addition of up to 3 reactant species, including a prevaporized liquid.

Gas samples are presently withdrawn through a new water-cooled convective quenched stainless steel probe with quenching gradient of greater than 2×10^7 K/sec. A quartz coated Platinum, Platinum-Rhodium thermocouple with water-cooled jacket is used to measure the longitudinal reactor temperature distribution. Sampling instrumentation is extended longitudinally through the reactor section along its center line.

Gas sample are presently withdrawn at up to twenty discrete longitudinal positions in the reactor and stored at low pressure in an all glass/teflon sampling assembly. Stable species including CO, CO₂, aldehydes, alkanes, and

other carbon containing species can be measured with a Hewlett Packard 7624 Research Gas Chromatograph System equipped with an electronic integrator and a modified catalyst for Flame Ionization detection. This approach permits identical sensitivity per gram atom of carbon for all carbon containing species ($\pm 1\%$ Precision). Hydrogen, oxygen and nitrogen compounds are determined by thermal conductivity ($\pm 3\%$ Precision).

B. Computer Modelling Efforts

Dr. Dryer has established relations with and received considerable cooperation from Drs. Chang and C. Westbrook of Lawrence Livermore Laboratory, Livermore, California (T Division). This group has been specifically interested in developing chemical kinetic modelling capabilities suitable for analytical experiments on combustion systems. A one-dimensional analytical model of the Princeton turbulent flow reactor and a thermodynamic chemical kinetic program have been developed and exercised.

The flow reactor model contains turbulent diffusion effects in the longitudinal direction but no turbulent chemical kinetic coupling.

To date detailed carbon monoxide and methane oxidation mechanisms have been assembled and used to test analytical programs. Results have confirmed that reactor turbulence has little effect on observed combustion chemistry and several interesting features regarding elementary kinetics have also been discovered. Of particular note modelling efforts for the carbon monoxide oxidation demonstrated reactions involving HO_2 and H_2O_2 were extremely important in reproducing the experimental results. For this reaction HO_2 reactions moderate OH concentration and thus slow down the oxidation of CO.

In the methane oxidation case, modelling efforts indicate that up to half the methane is oxidized via an ethane route due to recombination of methyl radicals. The ethane formed is then oxidized via ethane to formyl radicals and finally to CO. As fuel to air ratio increases this route plays an increasing role and under certain conditions, can dominate the oxidation mechanisms.

A joint paper (Westbrook 1977) on these results was generated and presented at an American Chemical Society Meeting (Physical Chemistry and Computers in Chemistry) held in New Orleans, March 20-25, 1977.

C. Paraffin Hydrocarbon Oxidation

Current work in this laboratory on the oxidation of paraffin hydrocarbons has been concerned with the lean oxidation of ethane and propane. The experimental work on ethane oxidation has been completed and semi-global expressions have been developed for the oxidation of ethane and ethene for the flow reactor conditions.

The general features of the lean oxidation of ethane have been presented elsewhere (see Cohen 1977) and will be only briefly summarized here. The oxidation of ethane is seen to proceed through three distinct regions. (See Fig. 1.) Ethane is first converted to ethene in a nearly isothermal region. This region is followed by a region in which ethene is converted to CO and finally in a third region CO is oxidized to CO₂.

During this contract period, work has concentrated on completion of the characterization of the first two regions in terms of our semi-global modeling efforts.

For the lean oxidation case, the first region contains two distinct zones. The first one is an autocatalytic zone for which the rate of ethane disappearance is dependent on the extent of reaction. The semi-global expression for this region is given by:

$$\frac{d[C_2H_6]}{dt} = -10^{14.38 \pm .28} \exp\left(\frac{-55250 \pm 2500}{RT}\right) ([C_2H_6]_0 - [C_2H_6])^{0.8} [C_2H_6]^{0.4} [O_2]^{-0.1}$$

for equivalence ratios between 0.04 and 0.25. (See Fig. 2.) Following the inflection of the ethane curve, the rate of ethane disappearance is represented by

$$\frac{d[C_2H_6]}{dt} = -10^{9.90 \pm 0.43} \exp\left(\frac{-45950 \pm 2110}{RT}\right) [C_2H_6]^{0.8}$$

The data and semi-global fit for this zone are shown in Fig. 3.

Semi-global modelling has also been applied to the second region where ethene is oxidized to CO. The semi-global rate for ethene disappearance is represented by

$$\frac{d[C_2H_4]}{dt} = -10^{14.96 \pm 0.23} \exp\left(\frac{-63840 \pm 1120}{RT}\right) [C_2H_4]^{1.05} [O_2]^{-0.1}$$

The data and semi-global fit for ethene are shown in Fig. 4.

With the lean oxidation of ethane well characterized, attention has turned to the lean oxidation of propane. Several experiments have been completed and some general insights have been gained.

As with ethane, the oxidation of propane shows three distinct regions. (See Fig. 5.) In the first region propane is isothermally converted to the olefins ethene and propene, followed by the oxidation of the olefin to CO and concluding with the oxidation of CO to CO₂. In contrast to ethane, no autocatalytic zone dependent on extent reaction has been observed in propane. Experiments are continuing to explore this point to determine the basis for this difference in the oxidation mechanism. Such considerations are only in a preliminary stage and developments will be reported in future reports.

D. Methanol Oxidation Studies

Studies of the oxidation of methanol have also been initiated since the contract began. A number of experiments have been conducted spanning a range of equivalence ratios between 0.05 and 3.15 and temperatures between 940 and 1030 K. Analysis of the results has initially involved extending the kinetic mechanism previously derived for pyrolysis of methanol. The methanol pyrolysis work has recently been presented at the American Chemical Society meeting (Physical Chemistry and Computers in Chemistry) held in New Orleans, March 20-25, 1977. A copy of this paper is included as Appendix A.

The results of a typical oxidation experiment for methanol are given in Fig. 6. Of particular note is the absence of methane and C₂ species which indicates that methyl radicals are not of major significance to the reaction mechanism. In addition it is interesting to note that appreciable CO₂ production does not occur until nearly all the methanol fuel has disappeared. This implies that either OH radicals are absent during the oxidation of the fuel or that reactions with OH and methanol or one of its primary products is much faster than the CO + OH reaction. This conclusion can be drawn from early work done on the moist oxidation of CO. (See Dryer 1971, 1973.)

These insights to the methanol oxidation mechanism represent our initial approach to this work since our studies are only three months underway. These observations serve as guideposts for future efforts and experimentation.

III. Future Goals

During the remaining three months of the present contract funding period the lean oxidation of propane and the methanol oxidation studies will be continued. These may include some sensitized reactions involving the CO/H₂O system. Work on the semi-global modelling of both the propane and methanol will be given further attention.

IV. Personnel

During the current funding period the following staff have been committed to the program:

Senior Personnel

1. Prof. I. Glassman 1/12 time
(S.S. 216-14-8327)
2. Dr. F. L. Dryer 1/4 time
(S.S. 060-36-8257)

Professional Research Staff

1. Dr. R. J. Santoro 1/3 time
(S.S. 024-34-9298)

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Cohen, R. S. 1977. "The High Temperature Pyrolysis and Oxidation of Ethane," Ph.D. Thesis, Department of Aerospace and Mechanical Sciences, Princeton University.

Dryer, F. L. and Glassman, I. 1973. "High Temperature Oxidation of Carbon Monoxide and Methane," The Fourteenth Symp. (Intl.) on Comb., 967, The Combustion Institute, Pittsburgh, Pennsylvania.

Dryer, F. L., Naegeli, D. and Glassman, I. 1971. "Temperature Dependence of the Reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$," Comb. and Flame, 17, 270.

Westbrook, C. K., Creighton, J., Lund, C., and Dryer, F. L. 1977. "A Numerical Model of a Turbulent Flow Reactor," Journal of Physical Chemistry, Proceedings of the Symposium on Reaction Mechanisms, Models and Computers, American Chemical Society, 173rd National Meeting, New Orleans, March 20-25, 1977 (to be published).

FIGURE 1

CHEMICAL COMPOSITION OF SPREAD ETHANE-AIR REACTION

ETHANE/OXYGEN OVERALL REACTION RATE
 FUEL LEAN RUNS—REGION I 950–1100K

ETHANE/OXYGEN OVERALL REACTION RATE
 FUEL LEAN RUNS - REGION II 1000-1150K

ETHANE / OXYGEN OVERALL REACTION STUDY
 ETHENE OXIDATION RATE FUEL LEAN RUNS 965 - 1150 K

FIGURE 5

FIGURE 6

Appendix A

KINETICS OF THE PYROLYSIS OF METHANOL

by

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Abstract

An adiabatic turbulent flow reactor was used to examine the pyrolysis of methanol in the temperature range 1070 K to 1225 K at atmospheric pressure. Emphasis has been placed on determining the important initiation and termination steps and estimating rate constants for several reactions. A steady state treatment of the proposed nineteen step mechanism yields a complex rate law for methanol decay. The roles of hydrogen as a promoter and methane as an inhibitor are accounted for in the proposed mechanism.

Kinetics of the Pyrolysis of Methanol

Introduction

Current concern over the dwindling global oil reserves has instigated research in alternative fuels. As one of the more attractive alternative fuels, methanol has continued to show promise in several economic and practical combustion studies.^{1,2} Aside from these studies there has been little information generated on the kinetics of combustion, with the exception of earlier low temperature work^{3,4} and some recent shock tube investigations.^{5,6}

From its simple molecular structure, one concludes that pollutant generation from methanol combustion should be limited to formaldehyde, carbon monoxide, unburned fuel and possibly some simple hydrocarbons. Whereas methanol vapor may result in toxicological problems similar to those of gasoline, the only pollutant having photochemical activity would be formaldehyde. The PAN derivative of formaldehyde is, however, not observed.

Methanol can be a more attractive fuel than gasoline because it has a higher octane number, a leaner flammability limit, and a higher flame speed. An additional advantage of methanol is that it can be converted to a mixture of carbon monoxide and hydrogen having a still higher flame speed and even wider flammability limits.⁷ The dangers, however, involved in the storage and transport of hydrogen hinder its use as a universal fuel. Methanol, on the other hand, with its relatively high heat of vaporization, flash point, and auto ignition temperature obviates these problems.

Research on the pyrolysis of methanol has been undertaken in this laboratory, therefore, with several purposes in mind. Pyrolysis results taken in the temperature range 1073 K - 1223 K should complement the existing low and very high temperature literature and act as a prelude to the more complex oxidation kinetics. Finally, a determination of the possibility of hydrogen

production from methanol should be ascertained.

Experimental

The pyrolysis reactions were performed at temperatures between 1073 K and 1223 K in an adiabatic turbulent flow reactor^{8,9} at atmospheric pressure. Methanol, of 99.9% purity (reagent grade) from J. T. Baker, Inc. was evaporated and then injected at the inlet section of the reactor duct (1 m x 10 cm) in concentrations between 0.6% and 1.2% and rapidly mixed (~ 3 m sec) with a carrier stream of nitrogen. Nitrogen samples were frequently taken to check for purity; less than 100 ppm of O_2 were found by gas chromatography (thermal conductivity using Carbosieve columns). In several experiments, methane or hydrogen of 99.97% and 99.95% purity respectively, both from the Matheson Co., Inc., was added at the inlet section. Product samples were withdrawn with a water cooled probe at up to twenty positions along the reactor duct and collected in glass sampling bottles. In addition, the temperature was concurrently measured during each run with a silica coated thermocouple to minimize heterogeneous reactions; in previous work wall reactions were also found to be negligible.⁹ Analysis of the contents of each bottle containing CO, CH_4 , C_2H_6 , C_2H_4 , HCHO and CH_3OH as well as C_2H_2 in trace quantities (< 50 ppm) was done using a Hewlett-Packard model 7620A FID-gas chromatograph (Porapak columns) adapted with a methanation catalyst as described elsewhere.¹⁰ H_2 was analyzed in a modified Hewlett-Packard TC-gas chromatograph.¹¹ Using a data reduction program, the raw data were smoothed by computer using a five-point parabola fit in order to calculate concentration time derivatives. Carefully note (see Figure 1) that with the exception of formaldehyde the smoothed values are virtually coincident with the raw data. When using this smoothing routine, data must be taken only from the central portion of the reaction zone since the accuracy of endpoint values is poor.

Results

To explain the experimentally observed product distribution (see Figure 1), the following mechanism is proposed:

This chain sequence which has many of the same features as Bowman's oxidation mechanism⁵ consists of initiation, Reaction 1; propagation, Reactions 2 through 10; transfer, Reactions 11 and 12; and termination, Reaction 13. In addition, Reactions 14 through 19 explain the formation of ethylene, and of acetylene.¹²

The methanol disappearance rate is shown to be

$$\frac{-d[\text{CH}_3\text{OH}]}{dt} = k_1[\text{CH}_3\text{OH}][\text{M}] + k_2[\text{OH}][\text{CH}_3\text{OH}] + k_6[\text{H}][\text{CH}_3\text{OH}] + k_7[\text{H}][\text{CH}_3\text{OH}] + k_8[\text{CH}_3][\text{CH}_3\text{OH}]$$

By using the steady state assumption, on all the radical species in the system, namely CH_3 , OH , H , CH_2OH , and HCO , one obtains the following rather complicated expression:

$$\frac{-d[\text{CH}_3\text{OH}]}{dt} = 2k_1[\text{CH}_3\text{OH}][\text{M}] + k_8 \left(\frac{k_1[\text{M}]}{k_{13}} \right)^{1/2} [\text{CH}_3\text{OH}]^{3/2} + (k_6 + k_7)[\text{CH}_3\text{OH}] \times$$

$$\left\{ \frac{(k_1[\text{M}][\text{CH}_3\text{OH}] + k_8 \left(\frac{k_1[\text{M}]}{k_{13}} \right)^{1/2} [\text{CH}_3\text{OH}]^{3/2} + 2k_4[\text{HCHO}][\text{M}] + k_{10} \left(\frac{k_1[\text{M}]}{k_{13}} \right)^{1/2} [\text{CH}_3\text{OH}]^{1/2} [\text{HCHO}] + k_{12} \left(\frac{k_1[\text{M}]}{k_{13}} \right)^{1/2} [\text{CH}_3\text{OH}]^{1/2} [\text{H}_2])}{(k_6[\text{CH}_3\text{OH}] + k_{11}[\text{CH}_4])} \right\} \quad (\text{A})$$

Note that Reactions 14 through 19 do not appreciably perturb the system since (i) all C_2 species are in low concentrations, (ii) H atoms are conserved, one being produced each time another is destroyed, and (iii) methyl radical reactions are relatively slow. Calculation of the rate of disappearance of methanol by Equation A (see Table 1 for rate constant expressions) is compared to the experimentally derived value for several runs in Figure 2. Agreement is surprisingly good considering that some rate constants had to be estimated.

In order to check our chain mechanism even further, the diluents, methane and hydrogen, were added in several experiments. Methane was found to decrease the rate of reaction (see Table 2) whereas hydrogen promoted reaction (see Table 3).

Discussion

The third term in Equation A, which represents hydrogen atom attack on methanol is predominant in this expression. This means that Reactions 6 and 7

are fast while Reaction 8 is relatively slow. This result is hardly surprising since H atom abstraction reactions are generally at least an order of magnitude faster than analogous methyl radical abstraction reactions. Thus, since H atom reactions are important to the propagation, Reactions 20 and 21 could reasonably contribute to termination:

Termination would proceed only negligibly by these routes if one can show that the rate of Reaction 20 is much less than that of Reaction 13. Estimates on the hydrogen atom and methyl radical concentrations are then needed. An upper estimate of the hydrogen atom concentration may be made by considering that the decomposition of methanol proceeds entirely by way of hydrogen atom abstraction of methanol. Thus:

$$[\text{H}] = \frac{1}{(k_6 + k_7)} \frac{1}{[\text{CH}_3\text{OH}]} \frac{d[\text{CH}_3\text{OH}]}{dt} \quad (\text{B})$$

The experiments carried out over the temperature range in this study show that the ratio $[\text{CO}]/[\text{CH}_4]$ varied from between fifteen and thirty. Reaction 7 therefore, appears to go about fifteen to thirty times as fast as Reaction 6, i.e., $k_7 \approx 15\text{-}30 k_6$. The H atom expression may be evaluated using experimental data and a known literature value for k_6 (see Table 1). A value of 6.503×10^{-13} moles/cc is obtained for the H atom concentration at the highest temperature (1223 K).

The methyl radical concentration is obtained from the rate of formation of all the C_2 products since the ethane which is initially formed may further react yielding ethylene and acetylene. Furthermore, Reaction 22 does not contribute appreciably to the methyl radical pool

because of the small concentration of ethane in the system and also because of the fact that the value of k_{18} ($3 \times 10^{16} e^{-88000/RT} \text{ sec}^{-1}$)²¹ is negligibly small in the temperature range of this study. Therefore:

$$[\text{CH}_3] = \frac{1}{k_{13}} \left[\frac{d([\text{C}_2\text{H}_6] + [\text{C}_2\text{H}_4] + [\text{C}_2\text{H}_2])}{dt} \right]^{1/2} \quad (\text{C})$$

At 1223 K, the methyl radical concentration is found to be 8.434×10^{-12} moles/cc.

An elegant method has been used before to take into account multiple termination steps.²² Assume that Reactions 13 and 20 both terminate the chain mechanism. Then by using the steady state assumption, necessitating a balance between the initiation rate and the termination rate, one can obtain:

$$k_{13}[\text{CH}_3]^2 + k_{20}[\text{CH}_3][\text{H}][\text{M}] = k_1[\text{CH}_3\text{OH}][\text{M}]$$

also

$$\frac{d[\text{H}]}{dt} = 0 = k_1[\text{M}][\text{CH}_3\text{OH}] + k_8[\text{CH}_3][\text{CH}_3\text{OH}] + 2k_4[\text{M}][\text{HCHO}] + k_{10}[\text{CH}_3][\text{HCHO}]$$

$$-k_6[\text{H}][\text{CH}_3\text{OH}] - k_{11}[\text{H}][\text{CH}_4] + k_{12}[\text{CH}_3][\text{H}_2] - k_{20}[\text{H}][\text{CH}_3][\text{M}]$$

Now let $\alpha = k_{13}[\text{CH}_3]^2 / k_1[\text{CH}_3\text{OH}][\text{M}]$, the fraction of termination that proceeds by methyl radical recombination. By substitution of α into the expression for the rate of hydrogen atom formation an equation of the form $A\alpha^{1/2} + B + C\alpha^{-1/2} + D(1-\alpha) = 0$ is obtained. If it is now assumed that Reaction 13 indeed dominates the termination process then $\alpha \approx 1$ and one can solve a quadratic equation for α . At 1223 K, the case where Reaction 20 should be most important $\alpha \approx 0.998$. The assumption that α is close to unity is valid, therefore, and it is verified that Reaction 13 is much more important than Reaction 20 with respect to the termination process.

It is apparent that, unless the H atom concentration is much greater than the CH_3 radical concentration, the rate of Reaction 21 is less than that of Reaction 20. Reaction 21 is wholly a three body recombination process whereas in Reaction 20 methane has several degrees of freedom to at least partially dissipate the enthalpy generated in the recombination. In view of the fact that the methyl radical concentration (8.434×10^{-12} moles/cc) is greater than the hydrogen atom concentration (6.503×10^{-13} moles/cc), it is concluded that Reaction 13 is the only significant contributor to the termination process in this scheme.

It may at first be puzzling that methyl radical recombination terminates the reaction scheme despite the fact that many hydrogen atoms are formed in the pyrolysis according to the given mechanism. To solve this paradox, it is necessary to postulate that Reactions 11 and 12 are important. It is only these transfer reactions that permit a build-up of CH_3 radicals relative to H atoms. In view of this argument it is interesting, yet not surprising, to note that the thermal equilibrium value for H atoms based on the entire mechanistic scheme is about 2×10^{-13} moles/cc (at 1223 K), only slightly below the experimentally derived upper limit (6.5×10^{-13} moles/cc). At this point a mechanistic explanation may be forwarded for the experimentally observed effects of the diluents hydrogen and methane on the system (recall Tables 2 and 3). As methane is added in larger amounts the pseudo-equilibrium of Reactions 11 and 12 is shifted in the direction governed by Le Chatelier's principle. More methyl radicals are formed as some hydrogen atoms are removed; this has a twofold effect. First, since methyl abstraction reactions are slower than hydrogen abstraction reactions, the chain reaction becomes slower. Second, with more methyl radicals in the system, increased termination decreases the overall radical pool and thus slows down the chain reaction. Contrariwise, one may envision an opposite effect when hydrogen is added.

Evaluation of Equation A has been made by assuming that Reaction 1 is the only significant contributor to initiation. There is little to choose between Reaction 1 and the alternative reactions:

except that Reaction 1 is expected to be thermodynamically favored. The heats of formation of Reactions 1, 23, and 24 are 91.5, 96.5, and 104.0 kcal/mole²³ respectively. Finally, it must be shown that Reactions 22 and 4 are insignificant. If Reaction 22 is included in the derivation of Equation A, it is found that the term $k_{22}[\text{C}_2\text{H}_6]$ cancels; hence, Reaction 22 has no effect on initiation.

According to the mechanism, formaldehyde should be formed in relatively high yields as an intermediate species, yet the concentration of HCHO remains very low (essentially steady state). The depleting Reactions 9, 10, and 5, which are much faster than the "unimolecular" decomposition of formaldehyde, Reaction 4, must be responsible for this. A reasonable estimate for $k_4[\text{M}]$ is $10^{14} \exp(-87,000/\text{RT}) \text{ sec}^{-1}$ where A is analogous²⁴ with that for $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}$ and $E \approx D_0(\text{H}-\text{CHO})$. A similar treatment for Reaction 1 gives $k_1[\text{M}] = 2 \times 10^{16} \exp(-91,000/\text{RT}) \text{ sec}^{-1}$.^{25,26} Note that according to the RRKM method for determining pressure dependence of a unimolecular process,²⁴ Reaction 1 appears to be in the pressure dependent region. At 1223 K, $k_1/k_{1\infty} < 0.5$ under the constraints that the collision diameter for deactivation $\sigma = 4.53 \text{ \AA}$, the collisional deactivation efficiency $\eta = 0.1$ and the pre-exponential dissociation factor $A_d = 2 \times 10^{16} \text{ sec}^{-1}$. If the rate of initiation is set equal to the rate of termination one obtains:

$$k_1 [M] = \frac{1}{[CH_3OH]} \frac{d([C_2H_6] + [C_2H_4] + [C_2H_2])}{dt}$$

A calculation of $k_1 [M]$ by the thermodynamic estimate gives 0.30 while the experimentally derived value from the above expression is 0.28 (both at 1175 K); the thermodynamic estimate therefore appears to be empirically reasonable. The ratio $k_4 [HCHO]/k_1 [CH_3OH]$ equals 5.216×10^{-3} (at 1223 K), indicating strongly that Reaction 4 does not appreciably contribute to initiation.

The steady state assumption, which is so important in the derivation of Equation A, is strongly supported by the agreement in Figure 2 between calculated and experimental results. Strongest support for the assumption, however, comes from a computer simulation of the kinetic scheme²⁷ where it is evident that the concentration of the significant radicals in the system change by no more than about an order of magnitude over the reaction zone (see Table 4). The time derivative of the concentrations are very close to zero and the steady state assumption is sufficiently good for these studies. From a mathematical standpoint alone, the effects of hydrogen and methane on the system may be explained by Equation A. Because the hydrogen concentration term appears in the numerator, but the methane concentration term appears in the denominator, it is corroborated that methane would decrease the reaction rate and hydrogen increase it.

It should be emphasized that the rate constants for Equation A have either been taken from the literature or derived on a thermodynamic basis. There has been no attempt made to artificially adjust rate constants to fit the experimental data. It is therefore extremely gratifying that the proposed mechanism fits the experimental data so well. It should be noted that better agreement could be obtained without making drastic changes in rate constant

values. There are at least two legitimate reasons for making slight changes in some rate constants. Certain values (such as k_{10}) are old and may be less accurate than values obtained with more sophisticated instrumentation. Moreover, other values (such as k_6) originally obtained near room temperature may be inaccurate when extrapolated to higher temperatures because of possible temperature dependence (curvature) in the pre-exponential factor.

It should also be noted that despite simple RRKM calculations for methyl radical recombination that place this reaction in the pressure independent region,¹¹ there have been some more accurate theoretical²⁸ as well as computational²⁷ studies that indicate the reaction to be in the falloff region in the temperature range of this study. A somewhat lower value for k_{13} would considerably improve the agreement between calculated and experimental values.

Conclusions

The pyrolysis of methanol does produce carbon monoxide and hydrogen in near equilibrium concentrations in the temperature range of this study. Despite some automotive investigations²⁹ indicating some complex hydrocarbon emissions from the combustion of methanol, the pyrolysis seems to lead to hydrocarbons no more complex than acetylene. Indeed in the oxidation, one would then expect even less hydrocarbon pollutant formation.

A consideration of key steps in the mechanism has explained the reaction product distribution and has led to a complex expression that is in good agreement with experiment. In the 1073 - 1223 K temperature range both hydrogen atoms and methyl radicals play key roles in the pyrolysis. Reactions 6 and 7 are the important propagating steps whereas Reaction 13 is the only significant termination step. This may be contrasted to both low and high temperature results. At low temperature, condensation reactions play the principle role in termination and the short-lived propagation is dominated by methyl radical

abstraction reactions. At high temperatures, the pyrolysis proceeds by way of hydrogen atom abstraction and terminates by hydrogen atom recombination. Here, a sort of transition region may be realized where the transfer reactions, 11 and 12, explain the otherwise paradoxical result of hydrogen atom propagation and methyl radical recombination.

Table I

<u>Reaction</u>	<u>Rate Constant</u>	<u>Reference</u>
1	$2 \times 10^{16} \exp(-91,000/RT) \text{ sec}^{-1}$	see text
4	$10^{14} \exp(-87,000/RT) \text{ sec}^{-1}$	see text
6	$1.3 \times 10^{13} \exp(-5340/RT) \text{ cc/mole-sec}$	13
7	15-30 k_6	see text
8	$1.8 \times 10^{11} \exp(-9800/RT) \text{ cc/mole sec}$	14
10	$1.78 \times 10^{11} \exp(-6600/RT) \text{ cc/mole-sec}$	15
11	$6.9 \times 10^{13} \exp(-11800/RT) \text{ cc/mole-sec}$	16
12	$3.4 \times 10^{11} \exp(-10340/RT) \text{ cc/mole-sec}$	17
13	$3 \times 10^{13} \text{ cc/mole-sec}$	18
20	$2 \times 10^{12} \text{ cc/mole-sec}$	19
21	$3 \times 10^{15} \text{ cc}^2/\text{mole}^2\text{-sec}$	20

Table II

Effect of Methane on Methanol Decomposition

<u>Reaction Progress</u>	<u>CH₃OH concentration (moles/cc)</u>	
	<u>Run 8 (T = 950°C)</u>	<u>Run 9 (T = 950°C, ~ 1%CH₄)</u>
	5.47x10 ⁻⁸	6.39x10 ⁻⁸
	4.19x10 ⁻⁸	5.98x10 ⁻⁸
	3.38x10 ⁻⁸	5.50x10 ⁻⁸
	2.84x10 ⁻⁸	4.91x10 ⁻⁸
	2.43x10 ⁻⁸	4.29x10 ⁻⁸
	2.04x10 ⁻⁸	3.84x10 ⁻⁸
	1.68x10 ⁻⁸	3.62x10 ⁻⁸
	1.41x10 ⁻⁸	3.47x10 ⁻⁸
	1.24x10 ⁻⁸	3.26x10 ⁻⁸
	1.10x10 ⁻⁸	3.04x10 ⁻⁸
	9.41x10 ⁻⁹	2.89x10 ⁻⁸
	7.37x10 ⁻⁹	2.78x10 ⁻⁸
	5.28x10 ⁻⁹	2.64x10 ⁻⁸
	3.30x10 ⁻⁹	2.45x10 ⁻⁸
	1.59x10 ⁻⁹	2.27x10 ⁻⁸
	4.21x10 ⁻¹⁰	2.10x10 ⁻⁸
	0	1.96x10 ⁻⁸

Table III

Effect of Hydrogen on Methanol Decomposition

<u>Reaction Progress</u>	<u>CH₃OH concentration (moles/cc)</u>	
	<u>Run 1 (T = 850°C)</u>	<u>Run 13 (T = 850°C, ~1% H₂)</u>
	6.68x10 ⁻⁸	3.52x10 ⁻⁸
	6.47x10 ⁻⁸	3.08x10 ⁻⁸
	6.18x10 ⁻⁸	2.75x10 ⁻⁸
	5.96x10 ⁻⁸	2.17x10 ⁻⁸
	5.80x10 ⁻⁸	1.88x10 ⁻⁸
	5.61x10 ⁻⁸	1.62x10 ⁻⁸
	5.39x10 ⁻⁸	1.43x10 ⁻⁸
	5.19x10 ⁻⁸	1.29x10 ⁻⁸
	5.08x10 ⁻⁸	1.18x10 ⁻⁸
	5.01x10 ⁻⁸	1.07x10 ⁻⁸
	4.94x10 ⁻⁸	9.43x10 ⁻⁹
	4.84x10 ⁻⁸	8.17x10 ⁻⁹
	4.71x10 ⁻⁸	7.04x10 ⁻⁹
	4.53x10 ⁻⁸	5.99x10 ⁻⁹
	4.33x10 ⁻⁸	4.92x10 ⁻⁹

TABLE IV

Radical Species in the Methanol Pyrolysis

(Concentrations in moles/cc)

<u>TIME</u> (msec)	<u>[H]</u>	<u>[OH]</u>	<u>[HCO]</u>	<u>[CH₃]</u>	<u>[CH₂OH]</u>
(20.85cm)					
3.363 E+1	2.945 E-12	2.699 E-12	4.700 E-14	9.345 E-11	1.115 E-8
4.860 E+1	4.479 E-12	3.628 E-12	5.988 E-14	9.361 E-11	1.335 E-8
6.358 E+1	6.332 E-12	5.074 E-12	6.912 E-14	9.200 E-11	1.453 E-8
7.858 E+1	8.752 E-12	7.218 E-12	7.622 E-14	8.899 E-11	1.488 E-8
9.359 E+1	1.214 E-11	1.038 E-11	8.273 E-14	8.460 E-11	1.453 E-8
1.086 E+2	1.719 E-11	1.515 E-11	9.093 E-14	7.874 E-11	1.359 E-8
1.237 E+2	2.514 E-11	2.247 E-11	1.046 E-13	7.124 E-11	1.217 E-8
1.388 E+2	3.746 E-11	3.33 E-11	1.286 E-13	6.201 E-11	1.037 E-8
1.539 E+2	5.256 E-11	4.569 E-11	1.617 E-13	5.187 E-11	8.364 E-9
1.690 E+2	6.210 E-11	5.269 E-11	1.845 E-13	4.302 E-11	6.438 E-9
1.842 E+2	6.219 E-11	5.177 E-11	1.846 E-13	3.650 E-11	4.826 E-9
2.007 E+2 (124.43 cm)	5.653 E-11	4.633 E-11	1.692 E-13	3.126 E-11	3.481 E-9

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FIGURES

Figure I. Methanol Pyrolysis, 1158 K
Reaction Product Distribution

Figure II. Equation A - Comparison of Calculated and Experimental
Results

Open circles are calculated points; closed circles are
experimental points.