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Combustion Characterization of Methylal in Reciprocating Engines

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Preface

This work was conducted by Southwest Research Institute (SwRI), San Antonio, Texas, under Subcontract No. AW-2-12266-1, Prime Contract No. DE-AC02-83CH10093, SwRI Project No. 03-5299 for the National Renewable Energy Laboratory (NREL), Golden, Colorado, and the U.S. Department of Energy (DOE), Washington, D.C. The contributions of technical monitors Brent K. Bailey and Christopher P. Colucci of NREL, John A. Russell of DOE, and subcontract administrator Ernest G. Oster of NREL are gratefully acknowledged. Further, contributions from the Musashi Institute of Technology (Musashi I.T.) in Tokyo, Japan, were essential to the conduct of Task 3, Hydrogen-Air Mixing Evaluation. The contributions of Katsuyoshi Koyanagi, Kimitaka Yamane, and Shoichi Furuhama are gratefully acknowledged. Susuma Ariga of SwRI helped to make the interaction with Musashi I.T. possible. Douglas Leone is greatly appreciated for his help in setting up the personal computer version of Chemkin-II, which was used in the chemical kinetics modeling work in Task 2. The patience and expertise of Ms. Janie Gonzalez in preparing this report are appreciated.

This effort consisted of three fairly autonomous tasks. The first task addressed cold-starting problems in alcohol-fueled, spark-ignition engines by using fine-spray port-fuel injectors to inject fuel directly into the cylinder. This task included development and characterization of some very fine-spray, port-fuel injectors for a methanol-fueled spark-ignition engine. After determining the spray characteristics, a computational study was performed to estimate the evaporation rate of the methanol fuel spray under cold-starting conditions and steady-state conditions. The second task was to perform a fundamental kinetic study of the autoignition characteristics of methylal, an oxygenated fuel that produces almost no soot in diesel engines, but, in contrast with most oxygenated fuels, has an excellent cetane number. The third task was to perform a computational study of fuel-air mixing in a hydrogen jet using a spark-ignited, hydrogen-fueled engine. The computational results were compared with experimental measurements being conducted at Musashi I.T. The hydrogen-air mixing work was directed at understanding the extreme sensitivity of ignition to spark plug location and spark timing in direct-injected, hydrogen-fueled engines.

The second task is discussed in this report. Tasks 1 and 3 are covered in NREL reports TP-425-6344 and TP-425-6346, respectively.

Executive Summary

Methylal, $CH_3OCH_2OCH_3$, is of interest as a fuel additive because it has been found to be very effective in reducing smoke emissions in diesel engines. It is unique among oxygenated fuels in that it has a low autoignition temperature and, therefore, a favorable cetane number. The objective of this study was to determine the important physical and chemical processes in the autoignition of methylal sprays at air temperatures and pressures typical in diesel engines. Basically, the objective was to provide a chemical kinetics model that would predict the ignition delay times of methylal sprays at compression ignition conditions.

Ignition delay times were measured in air at temperatures ranging from 690 K to 863 K with pressures ranging from 3.0 MPa to 3.9 MPa. Pyrolysis products of methylal were identified and measured over the same pressure and temperature range. The purpose of the pyrolysis experiments was to determine the chemical species of importance in the ignition mechanism. Both the pyrolysis and ignition measurements were performed at nearly constant gas density, i.e., a specific volume of about 65 cm^3/g. The pyrolysis and ignition delay experiments were performed by injecting methylal, in the form of a hollow cone spray, into a constant volume combustion bomb. The evaporation times were on the order of 1 millisecond (ms) or less, while ignition delay times ranged from 2.5 ms to 12 ms depending on the bomb temperature. Consequently, ignition delay times were attributed, for the most part, to a chemical induction period.

Based on these experimental measurements of the pyrolysis and ignition chemistry of methylal, researchers developed a kinetics model of methylal pyrolysis and oxidation chemistry. The chemical kinetics model was developed using Chemkin-II (Kee et al. 1991; Kee and Miller 1991.) Most of the kinetics data required for the chemical mechanism were obtained from the National Institute for Standards and Technology (NIST) Chemical Kinetics Database (Westley et al. 1993). However, no thermodynamic or kinetics data were available for methylal and several of its pyrolysis and oxidation products. The thermodynamic and kinetic data required for methylal and its pyrolysis products were calculated from first principles using the thermochemical kinetic approach outlined by Benson (1976).

The results of the chemical kinetics modeling were favorable. The model predicted reasonably accurate concentration-time profiles for the products formed in the pyrolysis of methylal. The ignition delay times were predicted within a few milliseconds of the measured values; e.g., at 863 K, the measured ignition delay time was $\approx$ 2.5 ms and the predicted value was 1.5 ms. This degree of accuracy was obtained throughout the experimental temperature range of 690 K to 863 K. It was concluded that chemical kinetics modeling is a viable method of predicting ignition delay times for low-molecular-weight fuels.

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Introduction

Methylal, $CH_3OCH_2OCH_3$, also known as dimethoxy-methane, is unique among oxygenates in that it has a low autoignition temperature, no carbon-carbon bonds, and is soluble in middle distillate fuels. Because of these properties, methylal has been shown to be a favorable fuel additive for reducing smoke in diesel engines. Recent measurements of ignition delay times indicate that methylal has a cetane number in the range of 45–50, which is compatible with diesel fuels. Engine tests have shown that adding methylal to diesel fuel significantly reduces smoke emissions. Gaseous emissions and combustion efficiencies obtained with methylal/diesel fuel blends remain essentially the same as those measured using neat diesel fuel. Lubricity measurements of methylal/diesel fuel blends with a ball on cylinder lubrication evaluator (BOCLE) show that methylal improves the lubricity of diesel fuel. Even though additions of methylal lower the fuel viscosity, the results of the BOCLE tests indicate that the methylal/diesel fuel blends cause less pump wear than neat diesel fuel.

The one drawback is that methylal has a low boiling point (42°C) and a relatively high vapor pressure. As a result, it lowers the flash point of diesel fuel and causes a potential fuel tank flammability hazard. One solution to this increased volatility is to make polyoxymethylenes with the general formula of $CH_3O(CH_2O)_xCH_3$ where $x > 2$. The molecules are similar to methylal, but have higher molecular weights and thus higher viscosities and substantially lower vapor pressures. Therefore, their flash points will be compatible with regular diesel fuel. The polyoxymethylenes are expected to have combustion properties similar to methylal. It is theorized that by analogy with hydrocarbons, the ignition quality (i.e., cetane number) of the polyoxymethylenes will be better than that of methylal. Also, the higher viscosities of polyoxymethylenes are expected to provide improved lubricity.

Background

One possible method of reducing particulate emissions in compression-ignition engines is to change the fuel. It is well known that fuel properties such as hydrogen content and molecular weight correlate with the tendency of a fuel to form soot. Several studies (Takahashi and Glassman 1984; Harris et al. 1986; Olson and Madronich 1985) have shown that the tendency of a fuel to form soot rises as the carbon-to-hydrogen ratio and the number of carbon-carbon bonds in the molecule increase. Studies in premixed flames (Takahashi and Glassman 1984) indicate soot formation correlates most strongly with the number of carbon-carbon bonds in the fuel. Fuels such as methane and methanol produce little or no soot because their carbon-to-hydrogen ratios are very low and they contain no carbon-carbon bonds. However, these fuels are relatively unsuitable for compression ignition engines because their cetane numbers are too low. On the other hand, regular diesel fuels, which have relatively high cetane numbers and ignite easily in a diesel engine, tend to form soot readily because they consist of high-molecular-weight hydrocarbons that contain several carbon-carbon bonds and a much higher carbon-to-hydrogen ratio.

There appears to be an exception to this trend in the substance known as methylal, $CH_3OCH_2OCH_3$. Methylal has a very low propensity to form soot because its combustion chemistry is similar to that of methanol. However, the ignition chemistry of methylal is quite different from other oxygenates. In a previous study of the flammability limits of alcohols and ethers, Naegeli and Weatherford, Jr. (1989) observed that methylal has a relatively low autoignition temperature. Methylal's autoignition temperature of 237°C (NFPA 1977), is low compared with 385°C for methanol; therefore, it is expected to have a much higher cetane number than methanol.

In a recent study, Naegeli (1992) evaluated methylal for use in internal combustion engines. Methylal appeared to be a good candidate as an additive for diesel fuel because it has a low autoignition temperature, burns soot free, and is completely miscible in middle distillate fuels. Naegeli (1992) performed experiments on methylal to determine its ignition quality and its effect on smoke emissions in diesel engines. Methylal ignition delay time was measured in a constant-volume combustion bomb at 1080°F and 530 psia of air. Methylal ignition delay times ranged from 2.3 ms to 2.8 ms.

Ryan (1985) and Ryan and Callahan (1988) showed that the cetane number of a test fuel could be predicted by comparing its ignition delay time with the ignition delays of fuel standards with known cetane numbers. Based on their correlations of ignition delay time with cetane numbers of petroleum-based diesel fuels, the authors predicted the cetane number of methylal to be about 49. This value was obtained by averaging the results of several ignition delay measurements. The individual cetane numbers measured for methylal ranged from 47 to 57.

Engine testing of methylal/diesel fuel blends in a Caterpillar 3306B DITA diesel engine showed significant reductions in smoke emissions. Figure 1 illustrates the effect of methylal on the exhaust opacity pulse produced at engine start-up. At engine start-up, the fuel/air mixture is especially rich, so the initial exhaust smoke opacity is particularly high. Similar but less dramatic results were obtained from opacity and smoke number data at the high-idle operating condition. Virtually no smoke emissions were observed when neat methylal was burned in the engine. These preliminary results indicated that methylal is an effective fuel additive for reducing particulate emissions in diesel engines.

Methylal is currently produced in limited supply for solvent use by the petrochemical industry. However, it is potentially available as a future fuel additive because it is synthesized from methanol and formaldehyde, which are readily available petrochemicals. Methanol is produced from a mixture of carbon monoxide and hydrogen, $CO + H_2$, or from producer gas made by reforming methane. While most methanol is currently made by reforming methane, several plants also have been developed to make methanol from the products of coal gasification.

Formaldehyde is currently produced by partially oxidizing methanol. Its synthesis is energy intensive because a significant fraction of the combustion energy in methanol is lost in the oxidation process. If formaldehyde could be made from producer gas by a catalytic process similar to that used to synthesize methanol, the production of methylal could become a more energy-efficient process.

The chemistry of methylal pyrolysis and oxidation is essentially unknown. However, the reactions of free radicals such as H and OH with methylal appear to be similar to those with methanol, formaldehyde, and dimethyl ether. In the present study, the rate constants for the reactions of free radicals with methylal were estimated by analogy from data on relatively well-known reactions. Unimolecular reactions of methylal and secondary products were calculated using the thermochemical approach outlined by Benson (1976).

Objective

The purpose of this study was to use experimental data on the pyrolysis and oxidation of methylal to create a better understanding of the autoignition process in diesel engines. The objectives were to measure pyrolysis products and ignition delay times over a range of pressures and temperatures applicable to diesel engines and to develop a chemical kinetic model of the pyrolysis and ignition mechanisms.

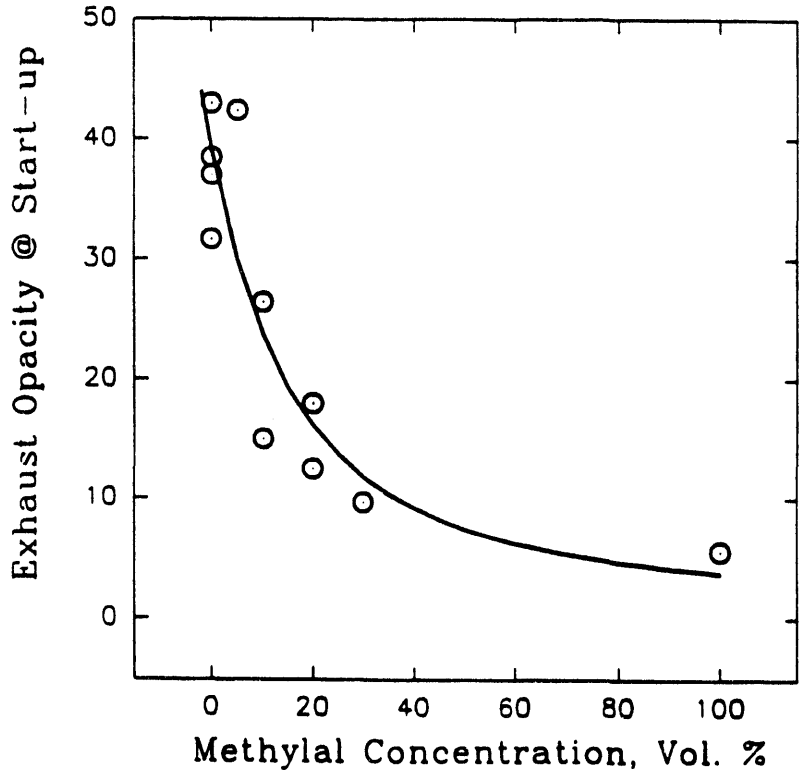

Figure 1. The effect of methylal concentration in DF-2 on the opacity of the start-up exhaust pulse.

Approach

The pyrolysis and ignition experiments were performed in a constant-volume combustion apparatus (CVCA) (Ryan 1985; Ryan and Callahan 1988), which had been previously designed to simulate the ignition process in a diesel engine. The CVCA shown in Figure 2(a) consists of a high-pressure vessel equipped with a diesel injector, a transducer to measure pressure variations, and thermocouples to measure temperature. Pressure variations accompanying the fuel-injection and ignition events were monitored and recorded with a Nicolet 2090 digital oscilloscope. Figure 2(b) is a more detailed drawing of the combustion bomb illustrating the spray pattern and the locations of the thermocouples (marked X) used to measure air temperature. Fuel was injected into the bomb in the form of a hollow cone spray (cone angle = 15°) using a Pintel type fuel injector. The hollow cone spray was used to produce a more even distribution of fuel vapor in the combustion bomb volume. Calculations indicated that the fuel spray from a solid cone spray injector would have too much momentum and would deposit on the opposite wall before evaporating.

Normally, the air temperature in the combustion bomb was determined as the average of the two thermocouples shown in Figure 2(b). As the temperature of the bomb increased, the temperature difference between these two thermocouples increased to as much as 50°C. In the present study, it was important to know the gas temperature as accurately as possible, so temperature measurements were also made along the centerline of the combustion bomb. This was done by removing the pressure transducer and inserting a thermocouple probe to different positions inside the bomb. A total of 125 measurements were made at five positions: five pressures ranging from 0.69 MPa to 3.5 MPa times five set temperatures ranging from 672 K to 901 K.

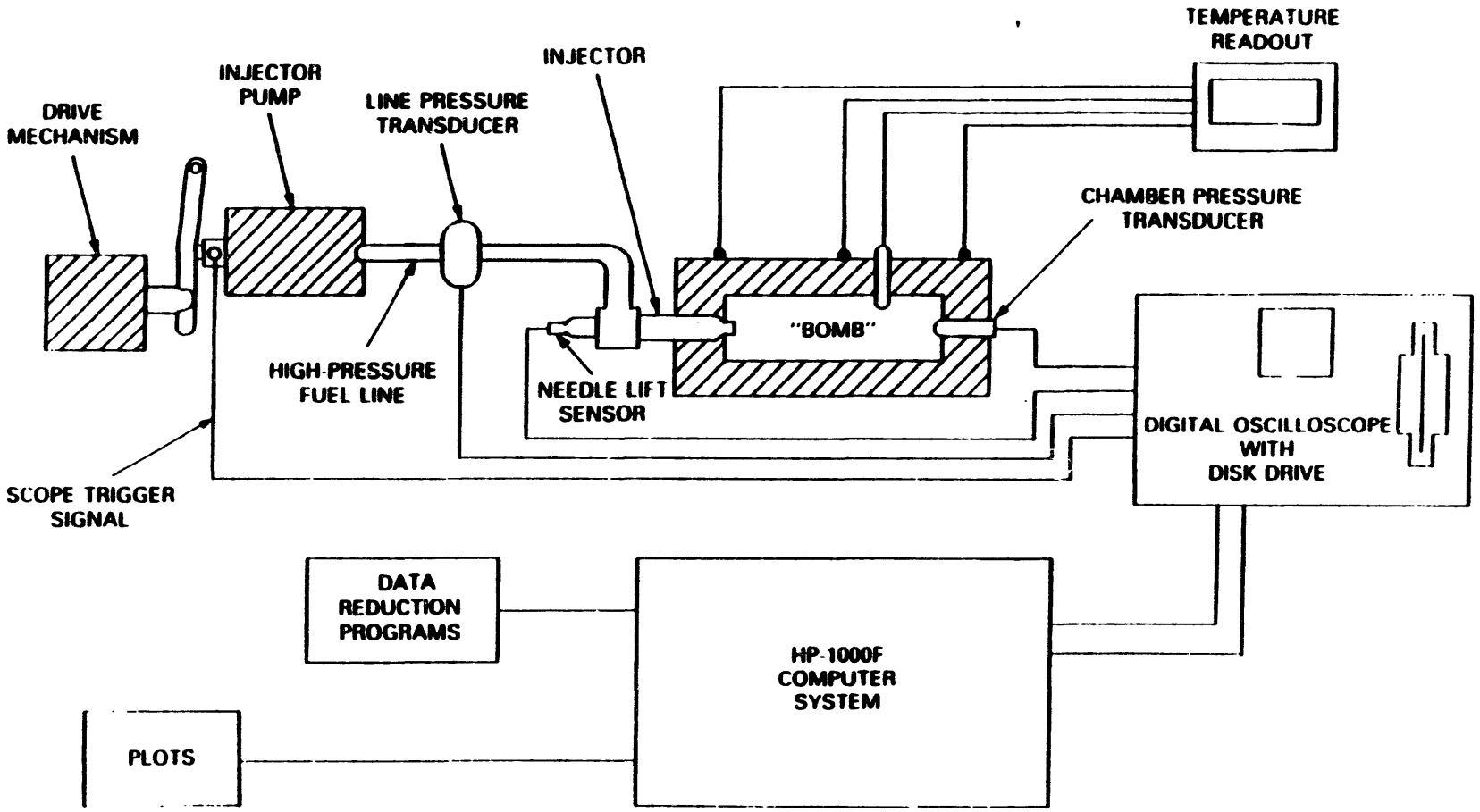

Figure 2(a). Constant-volume combustion apparatus (CVCA).

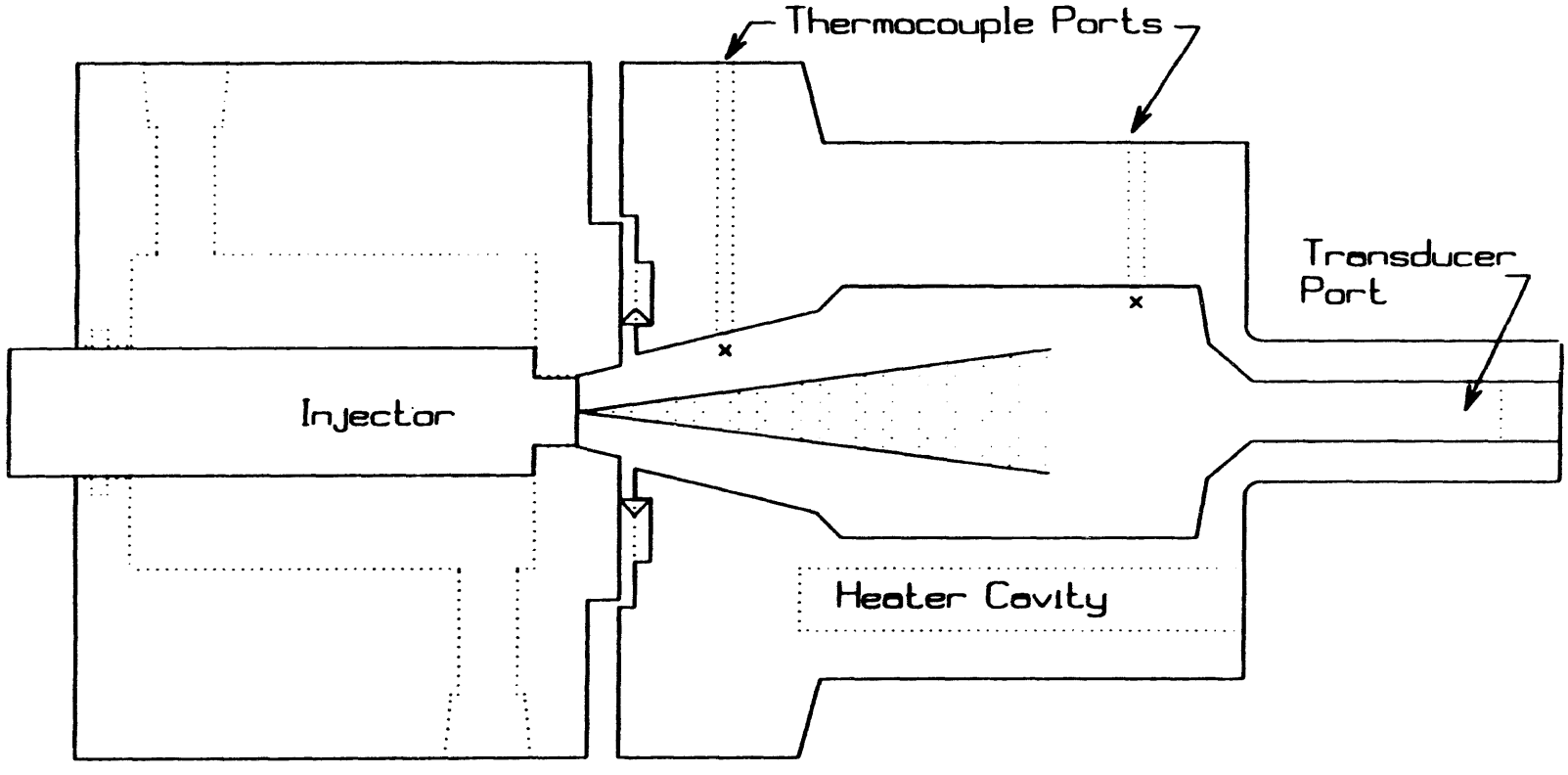

Figure 2(b). Schematic of the combustion bomb.

The results showed that the gas temperature in the central region of the bomb was within a few degrees of the average of the two thermocouples at the interior wall. Pressure had a small effect; temperatures increased about 6°C as the pressure decreased from 3.5 MPa to 0.69 MPa. Distance along the centerline had the greatest effect on the temperature. The measurements were made over a distance of 12.5 cm along the centerline of the bomb. The temperature was the highest at the center of the bomb. The drop-off on either side of the center ranged from 10°C to 15°C for the first 4 cm; beyond that point, the temperature decreased about twice as fast.

An attempt was made to correlate the temperatures measured at the centerline with the thermocouple readings at the wall, the position of the temperature probe, and the pressure. As it turned out, the temperature data along the centerline were more effectively used as a temperature table to interpolate the gas temperatures in the central region of the bomb where ignition appeared most probable.

Pyrolysis Experiments

Pyrolysis experiments on methylal were performed in the CVCA at temperatures ranging from 781 K to 863 K and pressures ranging from 3.5 MPa to 3.9 MPa. The experiments were performed by injecting about 70 mg of methylal into the helium-filled bomb. All the experiments were performed at the same specific volume, so the initial concentration of methylal was always about 0.8 mole percent at each temperature/pressure condition in the bomb. Helium was used in the pyrolysis experiments instead of nitrogen to simplify the chemical analysis of the products. Gas samples were extracted from the bomb at various times after the injection of methylal using a solenoid-operated Valcor gas sampling valve connected to a water-cooled, glass-lined sampling probe. The sampling valve opening and closing times were about 15 ms. The valve remained open for 50 ms while the gases in the bomb flowed into a 75-cm^3 collection vessel. Pyrolysis products were sampled at times ranging from 1 to 100 s depending on the temperature in the bomb.

Sample analysis was performed with a temperature-programmed Hewlett Packard gas chromatograph equipped with a thermoconductivity detector, a 0.125-in.-diameter/15-ft Hayesep DB packed column, and a helium carrier gas. Good resolution of the decomposition products, including carbon monoxide, methane, carbon dioxide, ethane, methanol, dimethyl ether, methyl formate, and methylal, was obtained by temperature programming the gas chromatograph. Hydrogen was detected in several of the samples, but was not measured quantitatively.

Ignition Delay Measurements

Ignition delay times were determined from the pressure changes that occurred when the fuel evaporated and began to burn. The pressure changes in the bomb were converted to changes in temperature using the ideal gas law. Figure 3 shows the temperature/time history of a typical ignition event. When fuel is injected, it must first evaporate before it ignites. The decrease in temperature (11.9°C) that initially follows the injection is caused by fuel evaporation and heating of the fuel vapors to the air temperature in the bomb. The duration ($\approx$ 2 ms) of this initial decrease in temperature is termed the physical delay. The overall ignition delay, including both physical and chemical processes, is determined as the time when the temperature rises above the initial air temperature in the bomb. Physical delays tend not to vary substantially because the droplet evaporation times for most fuels are similar. However, significant differences are observed in the overall ignition delay because the chemical kinetic times for ignition reactions depend strongly on chemical composition.

Ignition delay assessments were made at constant gas density over the temperature range of 690–863 K with pressures varying from 3.4 MPa to 3.9 MPa. Methylal was injected into air in concentrations of about 0.8 mole percent, producing an overall equivalence ratio of about 0.15. The methylal used in these

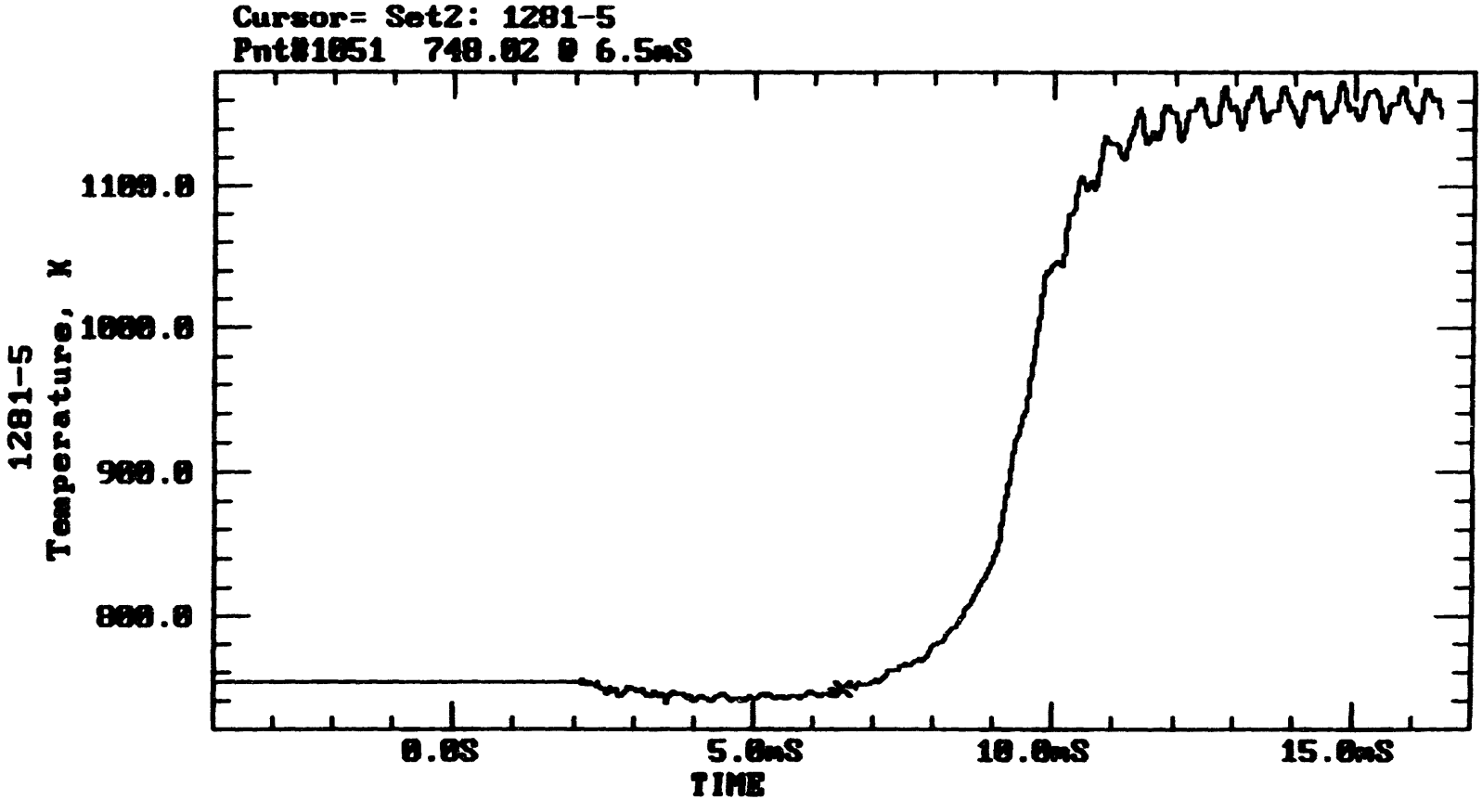

Figure 3. Temperature-time profile of ignition in the CVCA.

experiments was received free from Celenese Corporation. Celenese is the main supplier of methylal in the United States. The company expressed interest in methylal because of its potential use as fuel additive for reducing smoke in diesel engines.

Chemical Kinetic Modeling

Chemical kinetics modeling of the pyrolysis and ignition processes was performed using Chemkin II (Kee et al. 1991; Kee and Miller 1991). Chemkin II is a structured approach to the computational modeling of chemical kinetics and molecular transport in both static and flowing systems. In the present study, the personal computer version of Chemkin II was installed in a 486 DX-2, 66-MHz machine. An extended-memory Fortran compiler and linker was required to operate Chemkin II. Aside from being able to solve complex arrays of differential equations, interpret a chemical kinetics mechanism, and incorporate thermodynamic and transport data in the computations, Chemkin II includes an elaborate library of subroutines for solving problems involving chemical reaction and mass transport.

It is necessary to write an application program to use the program for a specific problem. Application programs were written for the Adiabatic Constant Volume case and Isothermal Constant Volume case. The basic input to the program is a thermodynamic data base and a chemical kinetic mechanism. For methylal, there were no chemical kinetic rate constants measured and no thermodynamic data available. The thermodynamic and chemical kinetic data on methylal and some of its pyrolysis and oxidation products had to be estimated.

Thermodynamic Properties

The thermodynamic data base, "Thermdat," used in Chemkin II has the same format as the data base used in the NASA chemical equilibrium code. The format contains the species name, type and numbers of atoms, physical state, molecular weight, and 14 constants used in polynomial expressions to calculate the heat capacity, enthalpy, and entropy. The first seven of these constants are used for temperatures ranging from 1000 K to 5000 K, and the second set of seven constants is used for temperatures ranging from 300 K to 1000 K. In either temperature range, the first five constants are used in a polynomial expression to calculate the heat capacity, C_p, at the absolute temperature T. The last two constants a_6 and a_7 are used along with a_1 through a_5 in Equations (2) and (3) below to calculate the enthalpy, H_T, and entropy, S_T, of the species at the absolute temperature T.

$$\frac{C_p}{R}=a_1+a_2T+a_3T^2+a_4T^3+a_5T^4 \qquad (1)$$

$$\frac{H_T}{R}=a_1T+a_2\frac{T^2}{2}+a_3\frac{T^3}{3}+a_4\frac{T^4}{4}+a_5\frac{T^5}{5}+a_6 \qquad (2)$$

$$\frac{S_T}{R}=a_1\ln(T)+a_2T+a_3\frac{T^2}{2}+a_4\frac{T^3}{3}+a_5\frac{T^4}{4}+a_7 \qquad (3)$$

Based on the results of the methylal pyrolysis experiments, it was concluded that, among the several species involved in the mechanism, there were no thermodynamic data available for the following species: methylal, $CH_3OCH_2OCH_3$; the methylal radicals, $CH_3OCH_2OCH_2$ and $CH_3OCHOCH_3$; methyl hydroperoxide, CH_3OOH; methyl formate, $HCOOCH_3$; the methoxy carbonyl radical, $COOCH_3$; the hydroxy carbonyl radical, COOH; and the formate radical, HCOO.

The heat capacities of the above-mentioned species were determined from a correlation of known heat capacity data for several oxygenated compounds over the temperature range of 300 K to 1500 K. Heat capacity data on 27 compounds were used to develop a correlation of heat capacity with temperature and chemical bond types. The expression derived from a nonlinear regression analysis of the heat capacity data was

$$C_p = C + k[N_{C-H}\exp(\frac{a}{T}) + N_{C-O}\exp(\frac{b}{T}) + N_{C=O}\exp(\frac{c}{T}) + N_{O-H}\exp(\frac{d}{T}) + N_{C-C}\exp(\frac{e}{T}) + N_{O-O}\exp(\frac{f}{T}) + N_{C=C}\exp(\frac{g}{T})] \quad (4)$$

where C_p is the heat capacity; T is the absolute temperature; N_{C-H}, N_{C-O}, $N_{C=O}$, N_{O-H}, N_{C-C}, N_{O-O}, and $N_{C=C}$ are the numbers of C-H bonds, C-O bonds, C=O bond, O-H bonds, C-C bonds, O-O bonds, and C=C bonds, respectively; and the constants in the equation are:

C = 0.571 k = 6.21 a = - 597.45 b = - 203.87 c = - 246.31

d = - 723.90 e = - 184.49 f = - 101.16 g = - 150.32

Equation (2) was used to calculate heat capacities of the species over a temperature range of 300 K to 1500 K. The constants a_1 through a_5 required for the "Thermdat" file were then determined by fitting the calculated heat capacities to a 4th degree polynomial function of temperature.

The enthalpies of formation and the entropies of the species were determined at 300 K by thermochemical methods using group additives (Benson 1976). Enthalpies of formation and entropies were then calculated over the temperature range 300 K to 1500 K via Equations (5) and (6).

$$H_T = H_{300} + \int_{300}^{T} C_p dT \quad (5)$$

$$S_T = S_{300} + \int_{300}^{T} \frac{C_p}{T} dT \quad (6)$$

The enthalpies of formation and entropies calculated using Equations (5) and (6) were then used in Equations (2) and (3), respectively, to evaluate the constants a_6 and a_7.

The parameters a_1 through a_7 were evaluated for each species at temperatures ranging from 300 K to 1000 K and from 1000 K to 1500 K. These parameters were then added to Thermdat. Thermodynamic data on other species including the methyl peroxide radical, CH_3O_2, and the methyl methylene ether radical, CH_3OCH_2, were obtained from the NASA-formatted Burcat data base (Gardiner 1984).

Chemical Kinetics

The reaction mechanism developed for the pyrolysis and oxidation of methylal is shown in Appendix A. The methane oxidation mechanism developed by Westbrook et al. (1977) was used as a starting point for the development of the chemical mechanism. The first step in developing the mechanism was to use the National Institute for Standards and Technology (NIST) Chemical Kinetics Database (Westley et al. 1993) to update all the rate constants for the reactions of H, CH_3, O, OH, and HO_2 radicals with H_2, CO, and

CH_4. Additional rate constants for reactions involving formaldehyde, CH_2O, methanol, CH_3OH, and the methyl peroxide radical, CH_3O_2, also were obtained from the data base.

Several new reactions involving the methyl peroxide radical (CH_3O_2) were added to the mechanism. It is important to note that peroxidic species are essential in the modeling of ignition and cool-flame chemistry. Appendix A is basically a copy of the input file to Chemikin II, showing the elements, chemical species, and reactions in the mechanism. The rate constant of each reaction is expressed as

$$k=AT^{n}\exp(-E_a/RT) \tag{7}$$

where A is the pre-exponential factor, n is the temperature exponent, R is the ideal gas constant, and E_a is the activation energy.

While developing the mechanism, no rate data were found in the NIST database for methylal ($CH_3OCH_2OCH_3$) or species such as methyl formate ($HCOOCH_3$) and the free radicals that were expected to form in the pyrolysis and oxidation of methylal. Rate constants for the reactions of radicals with methylal, dimethyl ether, and methyl formate were estimated by analogy with similar reactions involving methanol and formaldehyde. For example, there are two reaction paths for the OH radical to abstract an H atom from methylal. A primary H atom can be abstracted from the terminal methyl group via the reaction

$$CH_3OCH_2OCH_3 + OH = CH_3OCH_2OCH_2 + H_2O \tag{A}$$

or a secondary H atom can be abstracted from the central methylene group via

$$CH_3OCH_2OCH_3 + H = CH_3OCHOCH_3 + H_2O \tag{B}$$

The rate constant for Reaction (A) was estimated as twice the rate constant for the analogous Reaction C of OH radicals with methanol; i.e.,

$$CH_3OH + OH = CH_2OH + H_2O \tag{C}$$

The rate constant for Reaction (B) was assumed to be equal to that of the reaction of OH radicals with formaldehyde; i.e.,

$$CH_2O + OH = HCO + H_2O \tag{D}$$

By comparing Reactions A and C, we see that methylal has two terminal methyl groups while methanol has just one. Comparing Reactions B and D shows that methylal and formaldehyde have similar C-H bonds to a carbon atom that is also double-bonded to oxygen.

The unimolecular decompositions of methylal, methyl formate, methyl hydroperoxide, and the radical species CH_3OCH_2, $COOCH_3$, COOH, and HCOO were calculated using the Transition-State-Theory approach (Benson 1976). The major reaction paths for the decompositions of methylal, methyl formate, and methyl hydroperoxide were assumed to be

Methylal: $CH_3OCH_2OCH_3 = CH_3OCH_2 + CH_3$ (E)

Methyl Formate: $HCOOCH_3 = HCO + CH_3O$ (F)

Methyl Hydroperoxide: (G)$CH_3OOH = CH_3O + OH$ (G)

In each case, a carbon-oxygen bond is broken in the molecule. It is assumed in Reactions (E), (F), and (G) that the activation energies of the reverse reactions are zero. The reaction paths for the decompositions of CH_3OCH_2, $COOCH_3$, COOH, and HCOO radicals were assumed to be

$$CH_3OCH_2 = CH_3 + CH_2O \quad (H)$$

$$COOCH_3 = CO_2 + CH_3 \quad (I)$$

$$COOH = CO_2 + H \quad (J)$$

$$HCOO = H + CO_2 \quad (K)$$

In each case, a carbon-oxygen bond is formed in one of the product molecules. Benson and Jain (1959) concluded that the activation energy of the reverse of Reaction (H) is about 12 kcal/mole. The activation barrier of 12 kcal/mole in the reverse of Reaction (H) results from breaking one of the carbon-oxygen bonds in the CH_2O molecule. Because the reverse of Reactions (H), (I), (J), and (K) each involve the opening of a C=O double bond, their activation energies were assumed to be 12 kcal/mole.

According to Transition State Theory, the rate constant, k_{AB}, for the bimolecular reaction

$$A + B = AB^*$$

followed by

$$AB^* = AB$$

where AB^* is an activated complex in equilibrium with the reactants A and B, is given by

$$k_{AB} = \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \quad (8)$$

where k is the Boltzman constant, T is the absolute temperature, h is Planck's constant, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation. The rate constant, k_{AB}, may be calculated if ΔS^* is assumed to be the entropy change for the overall reaction and if ΔH^* is approximated as the activation energy of the reaction. Then the rate constant for the unimolecular decomposition of AB, k_{uni}, is given by

$$k_{uni} = \frac{K_{eq}}{k_{AB}} \quad (9)$$

where K_{eq} is the equilibrium constant for the reaction. Rate constants, k_{uni}, were calculated over a wide temperature range for Reactions (E), (F), and (G) assuming that $\Delta H^* = 0$ kcal/mole and for Reactions (H), (I), (J), and (K) assuming that $\Delta H^* = 12$ kcal/mole. These calculated rate constants were then fitted to Equation (7) using a nonlinear regression technique. Note that Equation (7) is the form used in the chemical mechanism input file to Chemkin II.

Results and Discussion

Pyrolysis

Pyrolysis experiments were performed to determine the important species and the most probable reaction paths for the decomposition of methylal. The results of the pyrolysis experiments are shown in Figures 4, 6, and 8. These figures show the concentration-time profiles of the most abundant species detected in the pyrolysis of methylal. In these figures, the concentration is given as a reduced mole percent. When methylal decomposes, the total number of moles, reactants and products included, increases. The reduced mole percent is the actual mole percent divided by the total number of moles of reactants and products.

When methylal decomposes, the major products are CH_4, CO, and CO_2. Hydrogen was not measured quantitatively, but an atom balance indicated that it may also be a major product. Two less abundant products that play an important role in the mechanism are methyl formate, $HCOOCH_3$, and dimethyl ether, CH_3OCH_3. Methyl formate was formed most readily at the highest temperature (863 K), while dimethyl ether was relatively more abundant at the lowest temperature (781 K). Trace amounts of formaldehyde, HCHO, and methanol, CH_3OH, also were observed. These observations provided the clues needed to develop the chemical mechanism given in Appendix A.

Figures 5, 7, and 9 show the predicted concentration-time profiles of the most abundant species calculated using Chemkin II and the mechanism in Appendix A for conditions of constant internal energy and constant volume. The mechanism predicts with reasonable accuracy the rate of methylal decomposition and the rate of methane formation. The mechanism underestimates the rates of formation of CO, CO_2, and dimethyl ether, and overpredicts the rate of formation of methyl formate. As a whole, the mechanism gives a reasonable ballpark estimate of the pyrolysis formation and decomposition rates. A better data base including a more thorough analysis of the pyrolysis products over a broader temperature range is required to formulate a more accurate mechanism.

Ignition

Calculated temperature profiles based on the mechanism given in Appendix A for the ignition of a stoichiometric methylal/air mixture are shown in Figure 10. It is interesting to note that Figure 10 shows a small temperature rise in the profiles that precedes the actual ignition event. The small initial rise in temperature is caused by the exothermic decomposition of methylal. This effect was not observed in the experiments because the overall equivalence ratio in the bomb was only 0.15.

Figures 11 and 12 compare the calculated ignition delay times with ignition delay times measured in the constant-volume combustion bomb. Figure 11 is a plot of the ignition delay time versus the absolute temperature, and Figure 12 is an Arrhenius type plot of the same data. The calculated ignition delay times are in good agreement with the measured values throughout the temperature range examined. Note that the calculated ignition delay times account for only the chemical delay. Although it may be fortuitous, the difference between the measured and calculated ignition delay times (1–2 ms) could be attributed to the physical delay time. Calculations indicate that fuel vaporization times are in the 1–2 ms range.

In the present study, it was assumed that an equivalence ratio of 1.0 is the most probable condition for ignition in the combustion bomb. However, because ignition delay time is dependent on both temperature and equivalence ratio, there may well be an optimum equivalence ratio in the bomb.

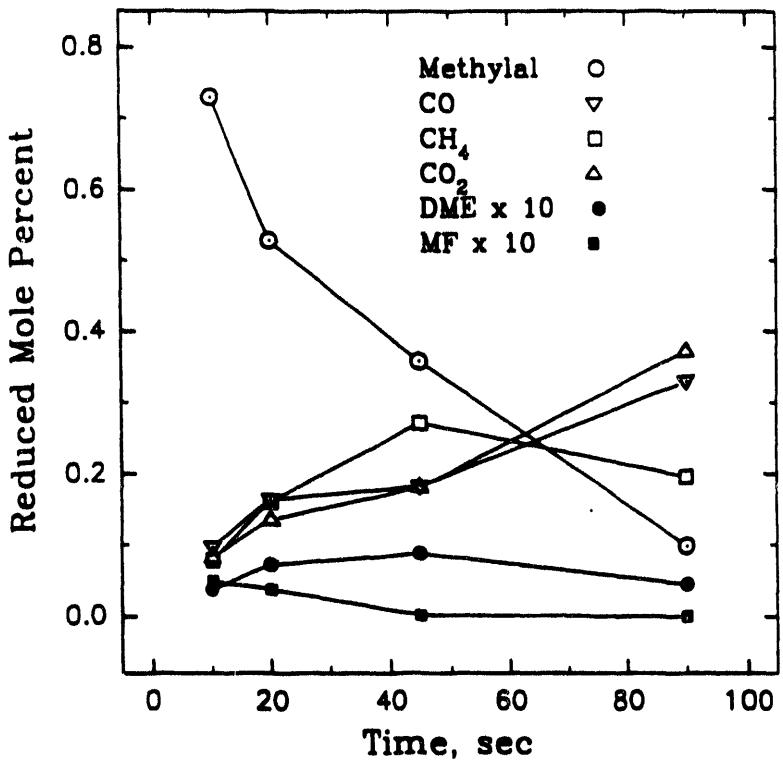

Figure 4. **Measured pyrolysis products formed from methylal in helium at a pressure of 3.52 MPa and a temperature of 781 K.**

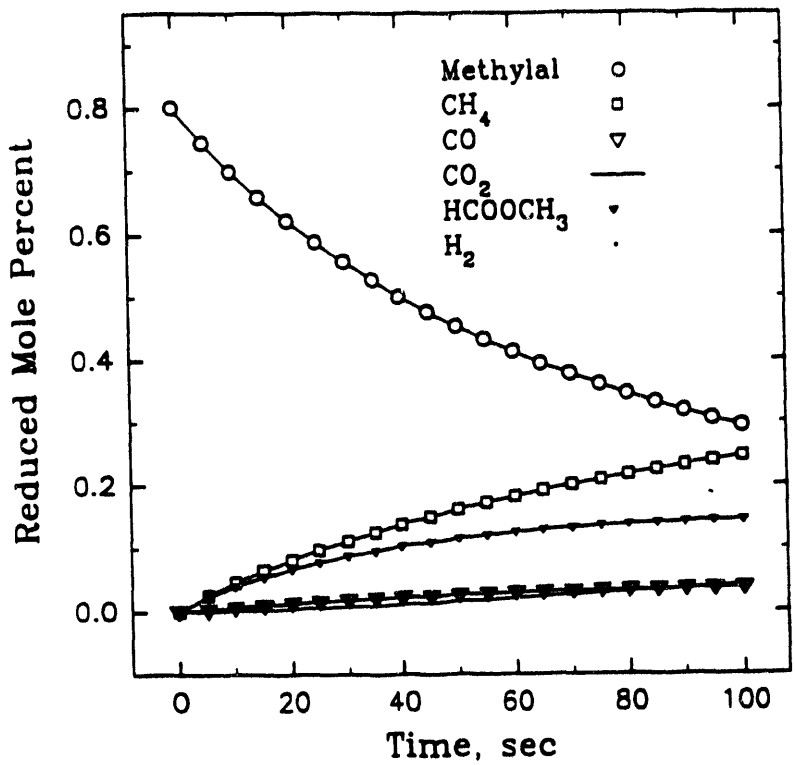

Figure 5. **Kinetic modeling results for the pyrolysis of methylal in helium at a pressure of 3.52 MPa and a temperature of 781 K.**

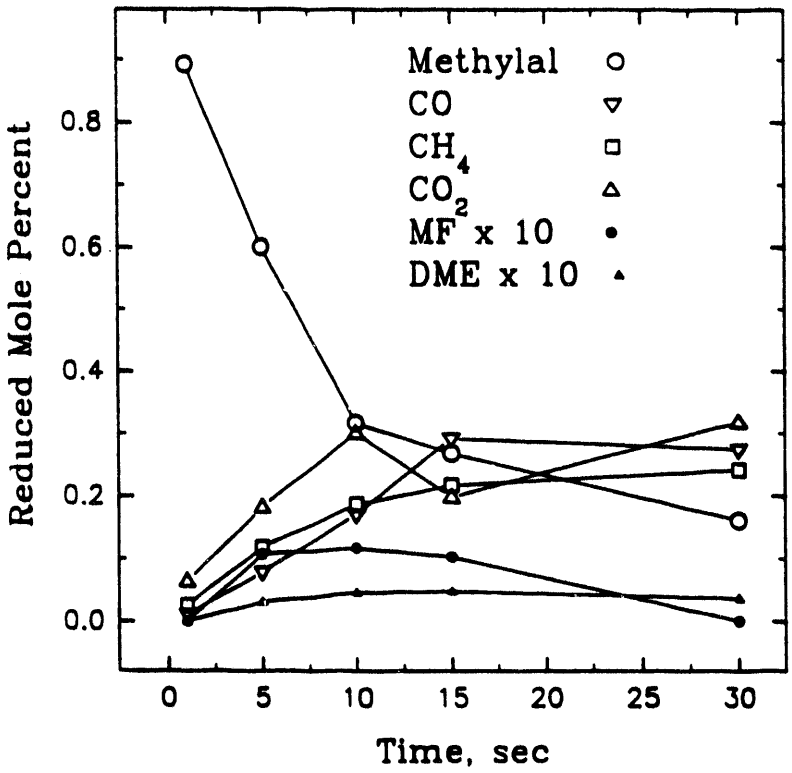

Figure 6. **Measured pyrolysis products formed from methylal in helium at a pressure of 3.67 MPa and a temperature of 816 K.**

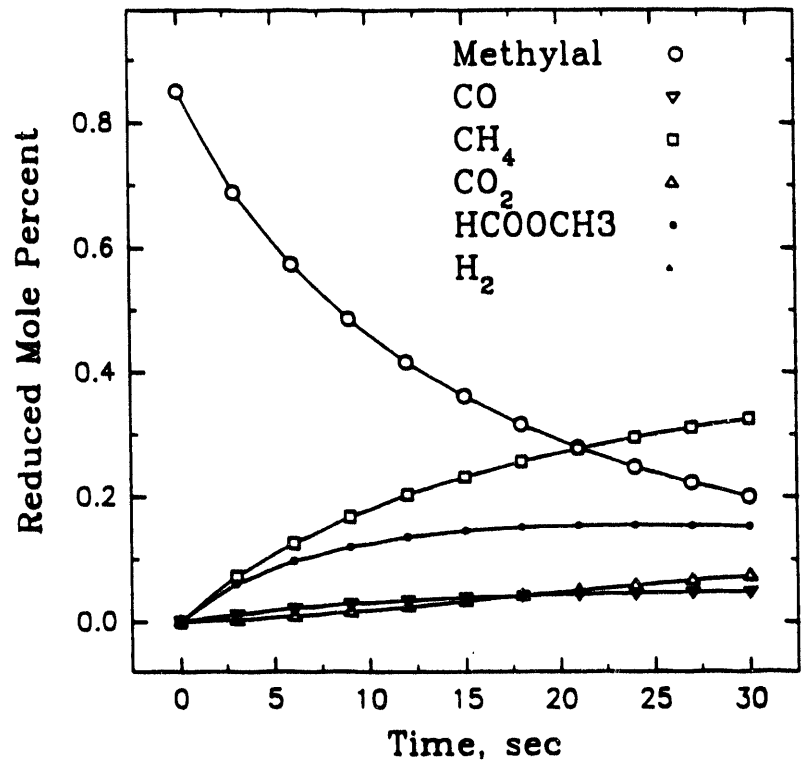

Figure 7. **Kinetic modeling results for the pyrolysis of methylal in helium at a pressure of 3.67 MPa and a temperature of 816 K.**

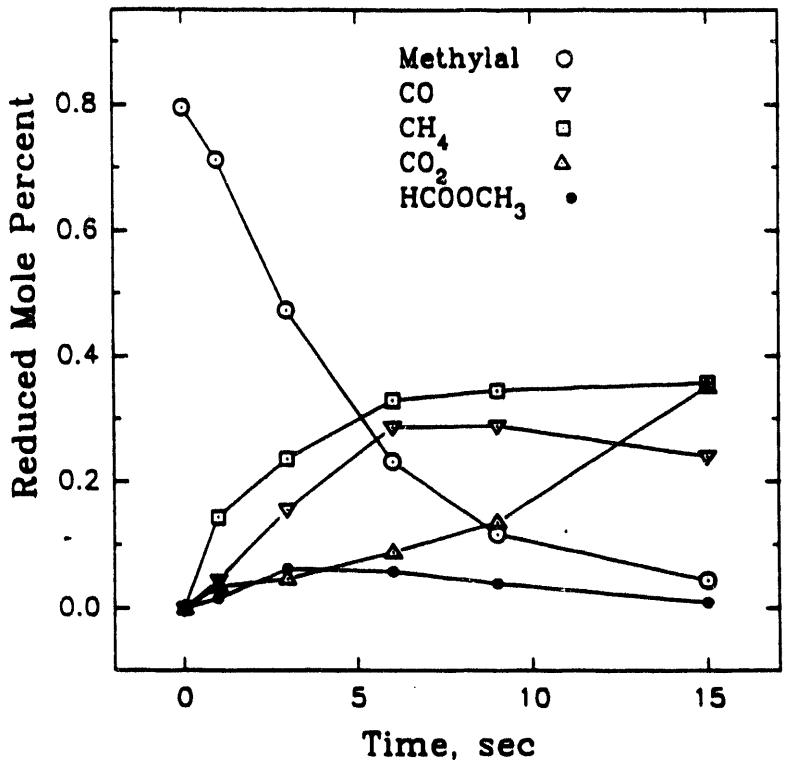

Figure 8. **Measured pyrolysis products formed from methylal in helium at a pressure of 3.89 MPa and a temperature of 863 K.**

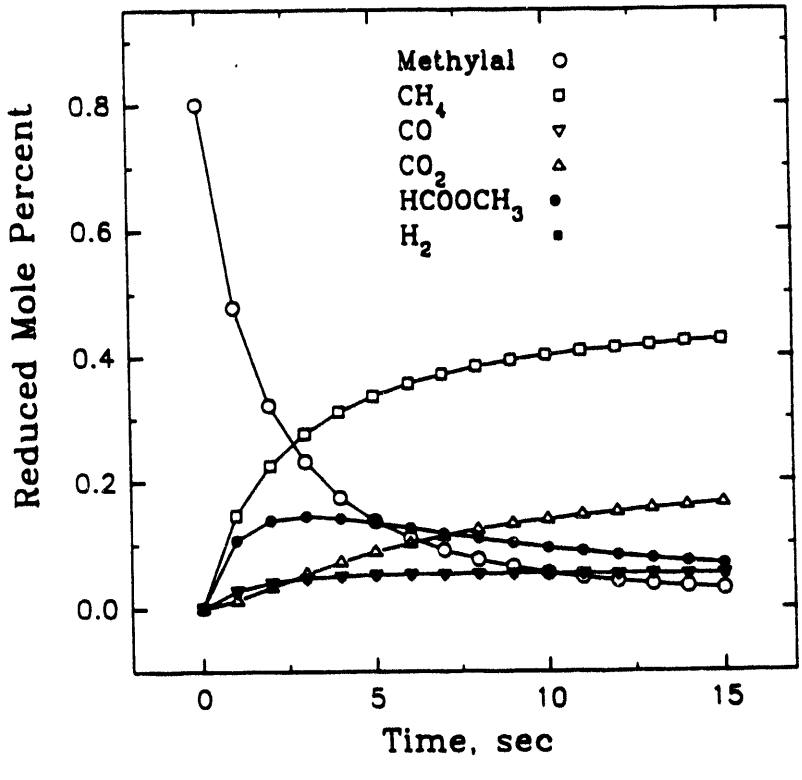

Figure 9. **Kinetic modeling results for the pyrolysis of methylal in helium at a pressure of 3.89 MPa and a temperature of 863 K.**

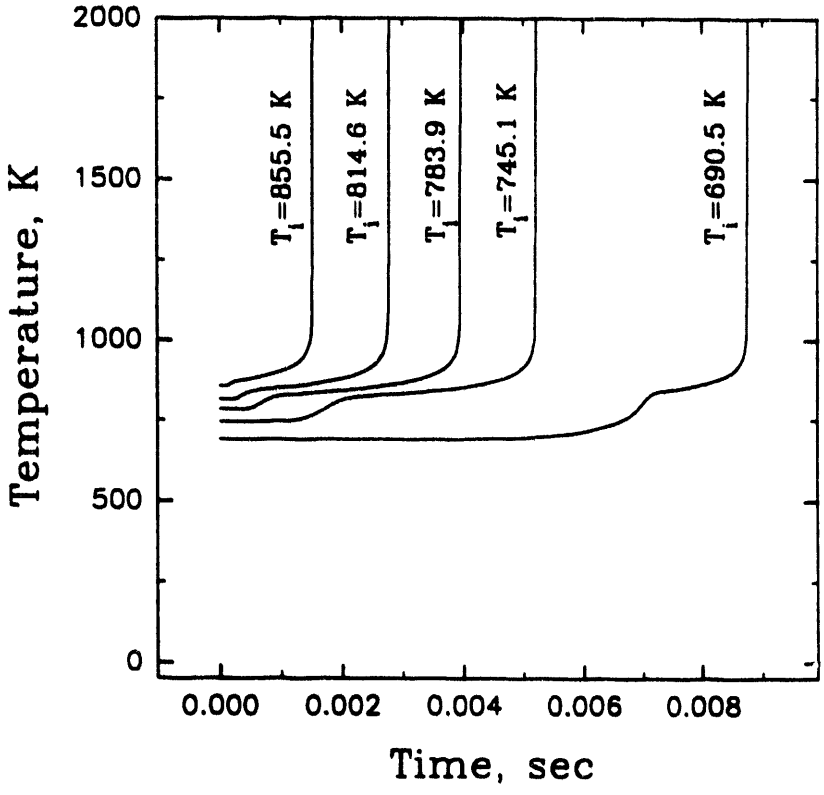

Figure 10. Calculated temperature profiles for the ignition of methylal in air for a specific volume of 62 cm^3/g.

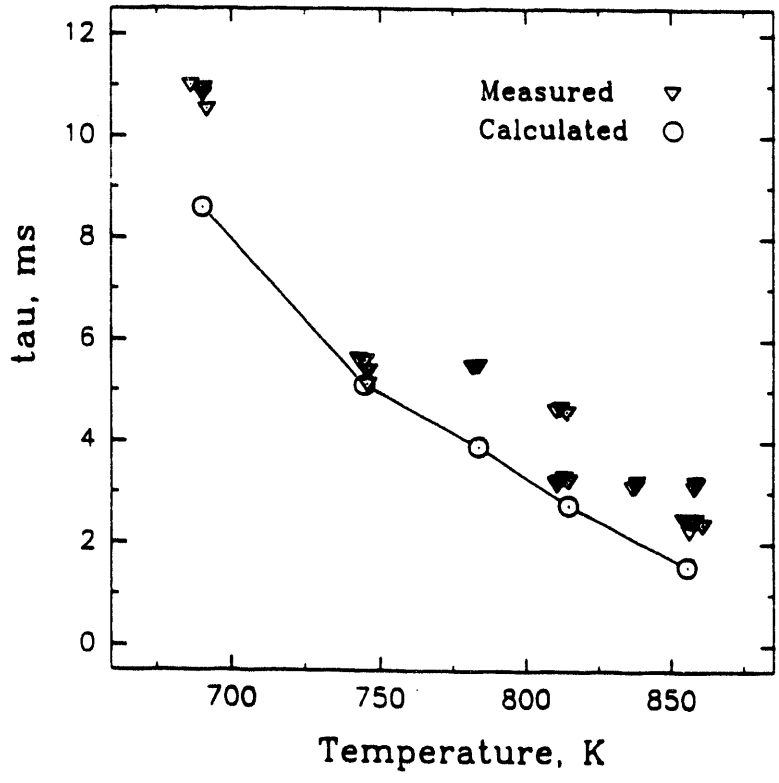

Figure 11. The effect of temperature on the ignition delay time, τ, of methylal.

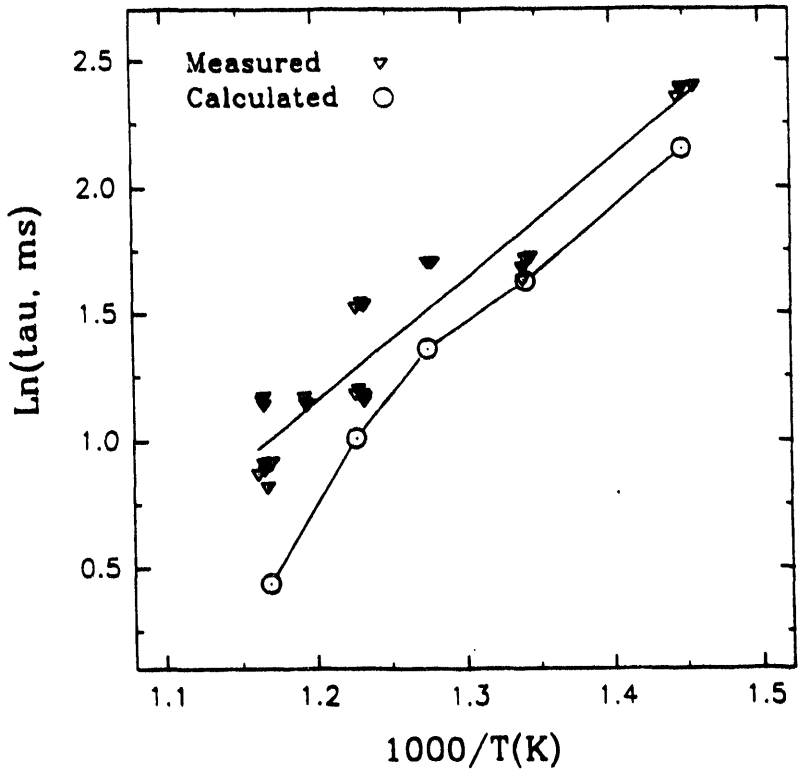

Figure 12. Arrhenius type plot of the ignition delay time, τ, of methylal.

When methylal was injected into the bomb, the overall equivalence ratio of the fuel/air mixture was 0.15; this caused the gas temperature to drop 11.9°C (see Figure 3). On this basis, the temperature drop for a stoichiometric mixture could have been as much as 79°C. It is probably even greater than 79°C because of the pressure rise that accompanies the phase change in the fuel.

When fuel is injected into the bomb, the temperature is expected to vary in regions where fuel droplets evaporate and mix with air. From this viewpoint, it is possible that autoignition actually occurs at temperatures significantly lower than the ambient air temperature in the bomb. When fuel is injected into the bomb, it evaporates and mixes with air, producing a wide range of equivalence ratios; i.e., the fuel/air mixture is very rich in some regions and very lean in others. In the fuel-rich regions, the temperature is lower because more fuel has evaporated and mixed with air in the bomb. Alternatively, the temperature of a lean fuel/air mixture is much closer to the ambient air temperature in the bomb.

Figure 13 shows the dependence of the calculated ignition delay time on the equivalence ratio. The calculations show that the ignition delay time increases quite rapidly as the equivalence ratio is reduced. There may be an optimum equivalence ratio for ignition in the combustion bomb. In regions of high equivalence ratio, the ignition delay time is expected to be relatively short. However, because the temperature of the fuel/air mixture is substantially lower than the ambient air temperature in the bomb, the actual ignition delay time is much longer. In regions of low equivalence ratio, the mixture temperature is not lowered as much so there is very little change in the ignition delay time. Basically, the optimum equivalence ratio could be determined by balancing the effects of equivalence ratio and temperature on ignition. Calculation of the optimum equivalence ratio was not attempted in this study, but will be considered in future work.

Conclusions

The purpose of this study was to develop a chemical mechanism for the pyrolysis and oxidation of methylal. Experiments were performed to determine the pyrolysis chemistry and ignition delay times of methylal fuel sprays at conditions comparable with those in compression ignition engines.

The pyrolysis of methylal yielded relatively high concentrations of methane, carbon monoxide, and carbon dioxide. Hydrogen also formed, but was not measured quantitatively. Significant amounts of methyl formate and dimethyl ether were produced, along with trace amounts of formaldehyde and methanol.

Methylal was found to have a relatively short ignition delay time compared to other oxygenated fuel. Ignition delay measurements were made in air at a specific volume of about 62 cm^3/g over a temperature range of 690 K to 863 K. Ignition delay times ranged from 2.3 ms at 863 K to 11 ms at 690 K.

A chemical kinetics mechanism was developed to predict pyrolysis and ignition of methylal. The mechanism gave reasonable estimates of the rate of decomposition of methylal and the rates of formation of the pyrolysis products. The mechanism gave a relatively accurate prediction of ignition delay times over the temperature range of experimentally measured values.

Methylal has autoignition characteristics compatible with diesel fuel. Recent ignition delay measurements indicate that its cetane number is in the range of 45–50. Methylal is soluble in diesel fuel in all proportions and is a good additive for reducing smoke emissions.

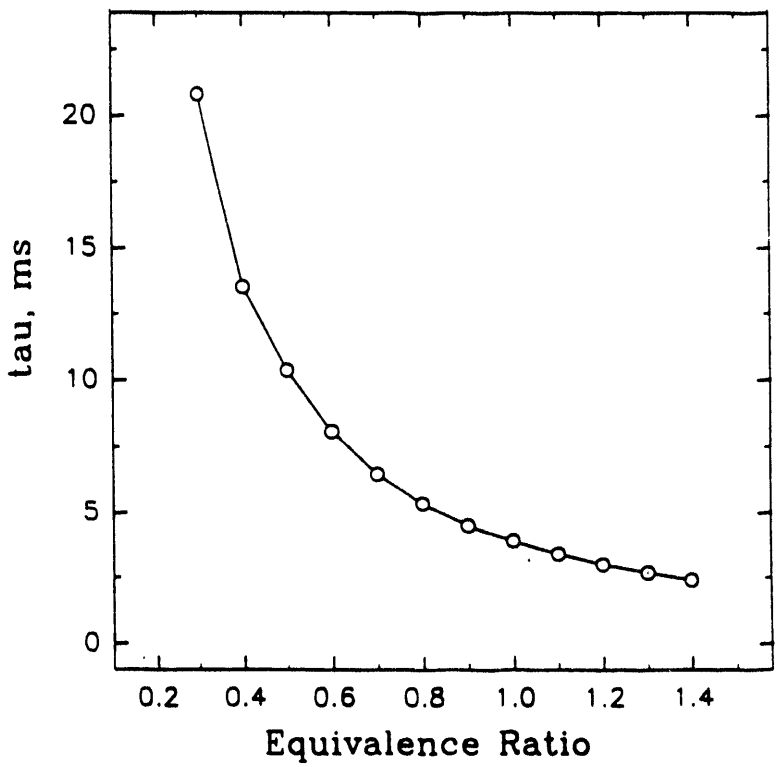

Figure 13. The effect of equivalence ratio on the calculated ignition delay time, τ, of methylal at 784 K and 3.37 MPa.

Recommendations for Future Work

Ignition of Gas Jets

SwRI recently has developed the capability to measure ignition delay times of gaseous fuels. These experiments are performed with a high-pressure natural gas type injector. Gas jets may be introduced into high pressure (3.5 MPa) air in as little as 2 ms. Autoignition of the gaseous fuel is detected as a pressure rise similar to the example shown previously in Figure 3. It is proposed that ignition delay measurements be made on hydrogen, methane, carbon monoxide, ethane, and ethylene gases. The measurements would be performed over a wide range of pressures and temperatures and the chemical kinetic model, which currently includes most of these molecules, would be used to calculate the measured ignition delay times. The results of this study would not only verify the basic rate data available for most of the above-mentioned molecules, but would also provide a useful kinetic model for predicting ignition delays of gaseous fuels in real systems.

Ignition Modeling

Several low-molecular-weight oxygenates and hydrocarbons have a potential use as fuels or fuel additives. The ignition and combustion chemistry of these fuels should be included in the kinetics model that has been developed for methylal. The model already includes the basic reactions for formaldehyde, methane, and methanol, in addition to methylal, so much of the framework is available for combustion of most fuels. However, more basic reaction rate data are required for the oxygenates. There are little or no rate data in the NIST Chemical Kinetics Database on oxygenates such as methylal, methyl formate, methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), methyl isopropyl ether, diethyl ether, dimethyl carbonate, and diethyl carbonate.

The first step in developing this data base is to examine the pyrolysis chemistry of oxygenated compounds. The pyrolysis experiments must be performed at high pressures (> 1.0 MPa) where the unimolecular and recombination reactions are essentially pressure independent. It is the high-pressure limiting rate constants that are most useful in real combustion systems. The experiments would be performed using very dilute mixtures of oxygenate in nitrogen. Rate constants could be calculated from first principles as was done in this study. The results of the pyrolysis experiments would be used first as a clue to important reaction paths and then as a rate measurement to compare with a kinetic model.

The second step would be to examine the low-temperature oxidation of oxygenated compounds. Both the pyrolysis and oxidation experiments would be performed in the same high-pressure apparatus. The results would be used to develop a kinetic model that would include several oxygenate fuels. The kinetic mechanism would be useful in engine models to predict combustion characteristics such as ignition delay and nitrogen oxides (NO_x) formation.

New Fuel Formulation

Previous work showed that methylal could be very compatible with diesel fuel if not for its low boiling point (42°C). Because methylal has a relatively high vapor pressure, there is a potential problem of deflagration, and possibly even explosion, of the ullage vapors in the fuel tank when it is blended with diesel fuel. In essence, methylal is a methyl end-capped formaldehyde polymer with the formula $CH_3O(CH_2O)_xCH_3$ where x = 1. It is well known that formaldehyde polymerizes easily. Therefore, control of the polymerization process and end capping with methyl groups could lead to a higher-molecular-weight fuel additive that would have physicochemical properties very similar to methylal.

In view of the volatility problem with methylal, future work is recommended to synthesize methyl end-capped polyoxymethylene polymers. The proposed study would also include bench-scale tests to determine combustion properties and full-scale engine tests to determine the additive's potential to reduce exhaust smoke. The latter would consist of mapping engine conditions, emissions, and performance in a medium-compression-ratio diesel engine.

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Appendix A

Reaction Mechanism for the Pyrolysis and Oxidation of Methylal

ELEMENTS
N O C H
END
SPECIES
C3H8O2* CH4 H2 CO CO2 CH3OCH3 HCOOCH3 CH3OH CH2O C2H6 C2H4 H2O O2 H2O2
CH3OOH OH HO2 H O CH3 CH3O CH2OH C2H5 CH3O2 HCO CH3OCH2 COOCH3
C2H6O2CH* C3H7O2* N2
END

REACTIONS	A	n	E
O2+M=O+O+M	1.82E+18	-1.0	118000.0
O2+H2=HO2+H	4.63E+13	0.0	56808.3
O2+HCO=HO2+CO	5.17E+08	1.3	-765.0
O2+C3H8O2=HO2+C3H7O2	4.1E+13	0.0	44906.0
O2+C3H8O2=HO2+C2H6O2CH	2.0E+13	0.0	38965.0
O2+CH4=HO2+CH3	3.97E+13	0.0	56887.8
O2+CH3OH=HO2+CH2OH	2.05E+13	0.0	44906.0
O2+CH2O=HO2+HCO	1.96E+13	0.0	38965.0
HCO+OH=CO+H2O	1.00E+14	0.0	0.0
H+O2=OH+O	2.19E+14	0.0	16790.0
H2+O=OH+H	1.82E+10	1.0	8900.0
O+H2O=OH+OH	6.76E+13	0.0	18360.0
H+H2O=OH+H2	9.33E+13	0.0	20370.0
O+H+M=OH+M	1.00E+16	0.0	0.0
CO+O+M=CO2+M	5.89E+15	0.0	4100.0
CO+O2=CO2+O	3.16E+11	0.0	37600.0
HCO+H=CO+H2	2.00E+14	0.0	0.0
HCO+O=CO+OH	1.00E+14	0.0	0.0
H+O2+M=HO2+M	1.66E+15	0.0	-1000.0
O+OH+M=HO2+M	1.00E+17	0.0	0.0
H+HO2=OH+OH	2.00E+14	0.0	900.0
H+H2O2=HO2+H2	1.70E+12	0.0	3780.0
OH+CO=CO2+H	2.73E+06	1.577	-799.6
OH+HO2=H2O+O2	5.01E+13	0.0	1000.0
OH+H2O2=H2O+HO2	8.90E+06	1.788	-813.1
OH+CH4=CH3+H2O	1.56E+07	1.8	2800.0
OH+CH3OH=H2O+CH2OH	6.68E+13	0.0	2806.0
OH+CH2O=H2O+HCO	1.17E+09	1.322	-283.1
OH+C3H8O2=H2O+C2H6O2CH	1.2E+09	1.322	-283.1
OH+C3H8O2=H2O+C3H7O2	1.34E+14	0.0	2806.0
OH+CH3OCH3=H2O+CH3OCH2	1.34E+14	0.0	2806.0
OH+HCOOCH3=H2O+COOCH3	1.2E+09	1.322	-283.1
H+CH3OH=CH2OH+H2	2.66E+13	0.0	6589.0
H+CH2O=H2+HCO	3.06E+10	0.956	3241.0
H+C3H8O2=H2+C3H7O2	5.3E+13	0.0	6589.0
H+C3H8O2=H2+C2H6O2CH	3.06E+10	0.956	3241.0
H+CH3OCH3=H2+CH3OCH2	5.3E+13	0.0	6589.0
H+HCOOCH3=H2+COOCH3	3.06E+10	0.956	3241.0

O+CH4=CH3+OH	1.00E+09	1.5	8600.0
O+CH2O=OH+HCO	5.36E+11	0.5633	2905.0
O+CH3OH=OH+CH2OH	1.72E+13	0.0	4913.9
O+C3H8O2=OH+C3H7O2	1.72E+13	0.0	4913.9
O+C3H8O2=OH+C2H6O2CH	5.36E+11	0.5633	2905.0
O+CH3OCH3=OH+CH3OCH2	1.72E+13	0.0	4913.9
O+HCOOCH3=OH+COOCH3	5.36E+11	0.5633	2905.0
CH3O2+H2=CH3OOH+H	3.01E+13	0.0	26029.7
CH3O2+CH4=CH3OOH+CH3	1.81E+11	0.0	18479.1
CH3O2+C2H6=CH3OOH+C2H5	2.95E+11	0.0	14942.2
CH3O2+CH3OH=CH3OOH+CH2OH	1.81E+12	0.0	13710.3
CH3O2+CH2O=CH3OOH+HCO	1.99E+12	0.0	11663.7
CH3O2+C3H8O2=CH3OOH+C2H6O2CH	1.99E+12	0.0	11663.7
CH3O2+C3H8O2=CH3OOH+C3H7O2	3.62E+12	0.0	13710.3
CH3O2+HCOOCH3=CH3OOH+COOCH3	2.0E+12	0.0	11663.7
CH3O2+CH3OCH3=CH3OOH+CH3OCH2	3.62E+12	0.0	13710.3
CH3+H2=CH4+H	1.93E+03	2.8	7876.5
CH3+HO2=CH3O+OH	1.81E+13	0.0	0.0
CH3+OH=CH2O+H2	3.2E+12	-0.53	10809.3
CH3+OH=CH3OH	2.23E+40	-8.2	11671.6
CH3+OH=CH3O+H	5.75E+12	-0.23	13928.9
CH3+O=CH2O+H	1.25E+14	0.0	2000.0
CH3+O2=CH3O+O	4.30E+13	0.0	30758.8
CH3+O2+M=CH3O2+M	5.80E+25	-3.3	0.0
CH3+O2=CH2O+OH	5.00E+11	0.0	10107.9
CH3+C3H8O2=CH4+C3H7O2	9.6E-01	3.721	6495.5
CH3+C3H8O2=CH4+C2H6O2CH	1.1E-03	4.854	3479.2
CH3+CH2O=CH4+HCO	1.1E-01	4.854	3479.5
CH3+HCO=CH4+CO	3.16E+11	0.5	0.0
CH3+HCOOCH3=CH4+COOCH3	1.1E-03	4.854	3479.2
CH3+CH3OCH3=CH4+CH3OCH2	9.6E-01	3.721	6495.5
CH3O+O2=CH2O+HO2	1.00E+12	0.0	6000.0
CH3O+CO=CH3+CO2	1.57E+13	0.0	11802.8
CH3O+C3H8O2=CH3OH+C2H6O2CH	1.02E+11	0.0	2980.5
CH3O+C3H8O2=CH3OH+C3H7O2	2.41E+11	0.0	7093.6
CH3O+HCOOCH3=CH3OH+COOCH3	1.02E+11	0.0	2980.5
CH3O+CH3OCH3=CH3OH+CH3OCH2	2.41E+11	0.0	7093.6
CH3O+CH3O=CH3OH+CH2O	6.03E+13	0.0	0.0
HO2+O=O2+OH	5.01E+13	0.0	1000.0
HO2+CO=CO2+OH	2.86E+14	0.0	24301.0
HO2+HO2=H2O2+O2	1.00E+13	0.0	1000.0
HO2+CH4=H2O2+CH3	2.00E+13	0.0	18000.0
HO2+CH3OH=H2O2+CH2OH	1.12E+12	0.0	13875.0
HO2+CH2O=H2O2+HCO	1.00E+12	0.0	8000.0
HO2+HCO=H2O2+CO	1.0E+14	0.0	0.0
HO2+C3H8O2=H2O2+C2H6O2CH	4.0E+12	0.0	12061.0
HO2+C3H8O2=H2O2+C3H7O2	2.2E+12	0.0	13875.0
HO2+HCOOCH3=H2O2+COOCH3	4.0E+12	0.0	12061.0
HO2+CH3OCH3=H2O2+CH3OCH2	2.2E+12	0.0	13875.0
H2+M=H+H+M	1.29E+15	0.0	101317.1
H2O+M=OH+H+M	1.68E+15	0.0	101217.8

H2O2=OH+OH	3.0E+14	0.0	48482.8
HCO+M=H+CO+M	1.18E+14	0.0	16009.3
CH2O=H+HCO	3.59E+14	0.0	89673.3
CH2OH=CH2O+H	7.0E+14	0.0	29634.1
CH4+M=CH3+H+M	2.00E+17	0.0	88400.0
CH3O=CH2O+H	7.05E+00	3.914	20267.4
CH3OOH=CH3O+OH	4.0E+15	0.0	42919.2
C2H6O2CH=HCOOCH3+CH3	4.52E+09	1.531	2377.2
C3H7O2=CH3OCH2+CH2O	3.71E+10	1.325	23226.0
COOCH3=CO2+CH3	9.85E+10	1.126	858.9
CH3OCH2=CH3+CH2O	3.47E+10	1.276	22102.8
HCOOCH3=HCO+CH3O	3.23E+09	1.609	102580.4
CH3OCH2+HCOOCH3=CH3OCH3+COOCH	31.1E-03	4.854	3479.2
CH3OCH2+C3H8O2=CH3OCH3+C3H7O2	9.6E-01	3.721	6495.5
CH3OCH2+C3H8O2=CH3OCH3+C2H6O2CH	1.1E-03	4.854	3479.2
CH3OCH3=CH3+CH3O	2.62E+16	0.0	82202.2
C3H8O2=CH3OCH2+CH3O	3.29E-18	11.276	74791.4
C2H6+CH3=C2H5+CH4	5.50E-01	4.0	8280.0
C2H4+O=CH3+HCO	3.16E+13	0.0	19400.0
C2H5=C2H4+H	3.80E+13	0.0	38000.0
C2H6+H=C2H5+H2	1.32E+14	0.0	9370.0
C2H5+O2=C2H4+HO2	3.16E+12	0.0	5000.0
C2H6+OH=C2H5+H2O	1.12E+13	0.0	2450.0
C2H6+O=C2H5+OH	2.51E+13	0.0	6360.0
CH3+CH3=C2H6	1.00E+13	0.0	0.0
END			

* Note that because species variables cannot be more than 10 characters in the reaction input file, methylal, $CH_3OCH_2OCH_3$, is written as C3H8O2 and the methylal radical species, $CH_3OCH_2OCH_2$ and $CH_3OCHOCH_3$, are written as C3H7O2 and C2H6O2CH, respectively.

DATE
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7/6/94

END