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TITLE **LASER-INITIATED CHAIN REACTIONS IN THE PARTIAL OXIDATION
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Laser-Initiated Chain Reactions in the Partial Oxidation of Methane

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ABSTRACT

Using laser photolysis of suitable precursor molecules to produce gas-phase free radicals, we have been studying important kinetic processes in the partial oxidation of methane. Prompt production of a relatively high concentration of free radicals via laser photolysis makes it possible to separate the thermal initiation step from the subsequent chain propagation steps. Since the conditions (temperature, pressure, and mixture composition) for rapid thermal initiation and optimum product production may differ, this provides an exciting potential application for laser-induced chemistry where the laser acts as the initiation source. We report our results on the partial oxidation of methane by oxygen at moderate temperatures. A trace amount of acetone is photolyzed at 193 nm as a prompt source of methyl radicals in methane-oxygen mixtures. Dramatic evidence of chain reaction processes is observed for laser initiation under experimental conditions where thermal initiation is not significant. Details of the proposed mechanism are discussed as well as application of the technique to technologies for methane conversion to transportable fuels such as methanol.

INTRODUCTION

Methane is a relatively abundant resource in some remote parts of the world including the north slope of Alaska; however, because of the difficulties of transporting it, much of this methane is now flared off at remote oil wells. There is considerable interest in converting this potentially valuable energy resource into a more easily transportable fuel. One approach to this is to convert the methane to methanol by partial oxidation using oxygen.

Experiments on the partial oxidation of methane by oxygen have been reviewed recently by Gesser, Hunter and Prakash¹. Much of the work involves the use of catalysis for the conversion process. Since impurities such as H_2S are frequently present in natural gas and because these impurities tend to poison catalytic surfaces, processes involving catalysis will probably have to clean up the natural gas first. Such a cleanup has serious consequences on the economic feasibility of a conversion process. An alternative which may avoid this problem is the homogeneous partial oxidation of methane by oxygen to produce methanol.

At high temperatures, the homogeneous gas phase oxidation of methane by oxygen produces a flame as the methane burns

with water and carbon dioxide as products. At lower temperatures, it is possible to control the oxidation to produce methanol as a product. Production of methanol and carbon monoxide has been observed in the thermally-initiated partial oxidation of methane at both high pressures (up to 50 atmospheres)² and near 1 atmosphere pressure³.

For the thermally-initiated oxidation of methane, the initiation reaction which produces free radicals is

The important chain propagation steps at early times in the chain and at moderate pressures are

Methyl radicals undergo reaction with oxygen via reaction 2 to produce methyl peroxy radicals. The methyl peroxy radicals then react with methane to produce methyl hydroperoxide and a methyl radical via reaction 3 creating a linear chain process. If the temperature is high enough, the methyl hydroperoxide undergoes unimolecular decomposition to produce a methoxy radical and a hydroxyl radical via reaction 4.

The methoxy radicals can then react via the following reactions to produce either methanol or formaldehyde:

These reactions (5, 6, and 7) are the primary removal steps for methoxy radical and are the primary production channels for the formation of methanol (via reaction with methane) and formaldehyde (via reaction with oxygen and thermal decomposition) in the chain process. Since each reaction of methoxy produces another radical, the chain continues to propagate. Since more than one radical is created by each pass through the chain, this is a branching chain with gain for each pass. Competition between these three reactions will determine the relative yield of methanol and formaldehyde production in the reaction. The OH, HO₂, and H atoms produced are converted into methyl radicals by the following reactions:

The methyl radicals then undergo reaction with oxygen via reaction 2 and the chain proceeds. Under some conditions, such as high pressure and high temperature, the radical concentration becomes large and radical-radical reactions involving CH_3 , CH_3O_2 , and HO_2 will become important sources of methoxy radicals as well via the following reactions⁴:

Since one radical is produced for each radical consumed in this sequence of reactions, the chain reaction is a linear chain under these conditions.

Termination steps in the chain reaction include radical losses by diffusion to the reactor walls and radical-radical reactions such as the following:

Under the conditions of the experiments reported here, losses by diffusion to the reactor walls probably dominate. A detailed discussion of radical-radical processes is probably not important for understanding our experiments and is beyond the scope of this paper.

Both the time scale and product yields of the chain reaction are sensitive to the temperature, the pressure of methane, and the pressure of oxygen. The thermal initiation step, reaction 1, has an activation barrier of 56.9 Kcal/mole⁴ and is thus very sensitive to temperature. Two reactions in the chain propagation appear to be rate limiting, at least in the limit of low radical densities. Reaction 3 has a barrier of only 18.5 Kcal/mole but a relatively small Arrhenius pre-exponential A factor of $3. \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁵ This reaction may be rate limiting at moderate pressures. Reaction 4 has a high barrier of 42.9 Kcal/mole. At low temperatures, the decomposition of methyl hydroperoxide by reaction 4 is the rate limiting step. For temperatures where this reaction is very slow, the chain reaction will be a linear chain producing methyl hydroperoxide. At higher temperatures, the chain reaction will be a branching chain producing 3 radicals for each pass through the chain. The reaction products expected under these circumstances are CH₃OH, CH₂O, and H₂O. The formaldehyde produced may undergo

further oxidation to produce CO. Under conditions which produce high radical concentrations, radical-radical reactions to produce methoxy radicals may become the most important chain propagation steps.

For the thermally-initiated chain reaction to produce methanol, temperatures in the range of 450 C have been reported.³ At these high temperatures, complications due to competing reactions within the chain (for example, between reactions 5,6, and 7) and the further oxidation of methanol become important and lead to a lower yield of desirable products.

In a chain process, the time required to produce a significant amount of product is a function of the rate of initiation, the chain length, and the time required for one pass through the chain. Normally, the temperature must be kept reasonably high to maintain a sufficient rate of initiation and hence product formation. However, by using non-thermal initiation (such as laser photolysis) as a source of radicals, the rate of initiation is then independent of temperature, and it may be possible to carry out the reaction under milder conditions (temperature, pressure, etc.) where the product yields may be quite different from those expected using conditions necessary for thermal initiation.

Laser-initiated chain reactions have been demonstrated for a number of systems. Hill and Laguna demonstrated that methane/oxygen/SF₆ mixtures could be detonated using the output of a CO₂ laser.⁶ Nesbitt and Leone have studied the chain reactions at room temperature of chlorine atoms in H₂S, in H₂, and in CH₃SH.^{7,8} Bray and Chou have reported the synthesis of cumenehydroperoxide and t-butylhydroperoxide in the 100-150 C temperature range using ultraviolet laser initiation.⁹ Reddy has demonstrated that methyl chloride can be produced by the laser initiated chain reaction of Cl atoms and methane¹⁰ and Nesbitt and Leone have studied laser initiated chain reactions of Cl atoms with n-butane and ethane using infrared fluorescence of the vibrationally excited reaction products to follow the chain reaction.¹¹ Wolfrum and Schneider have demonstrated the formation of vinyl chloride and vinylidene fluoride by ultraviolet laser induced chain reactions.¹² Recently, Lavid and Stevens have observed photochemical ignition of H₂/O₂ mixtures using excimer lasers.¹³

In this paper, we present the results of our preliminary studies on laser-initiated chain reactions in the partial oxidation of methane by oxygen at temperatures in the 400-450 C range. The primary goal of these experiments was to demonstrate a laser-initiated chain reaction in the partial oxidation of methane by oxygen under conditions in which

thermal initiation did not lead to a significant amount of reaction.

EXPERIMENTAL

The basic experimental apparatus is shown schematically in Figure 1. The reactor consists of a 22 mm i.d., 26 mm o.d. quartz tube through which methane and oxygen flow. Suprasil quartz windows are fused at right angles to the gas flow for transmitting the photolysis laser light into the reactor for laser-initiated experiments. The cell is heated in three zones using commercial clamshell heater elements which consist of helically wound wire (chromium, aluminum, iron alloy) embedded in a ceramic structure. The cell sits within these elements and the elements are wrapped with fiberglass tape and surrounded by Fiberfrax insulation to minimize heat loss. Temperatures are measured with a thermocouple which can be moved so as to probe various locations within the reactor. The temperatures are controlled using simple variable transformers.

The methane is preheated in a 30 cm long zone. The oxygen is introduced through a variable length 6 mm diameter quartz tube into the flow reactor. In most experiments, the oxygen is introduced approximately 2.5 cm upstream from the windows. The methane and oxygen then flowed a distance of 30 cm through the heated zone. The reaction is then quenched by collisions

with a water cooled tube at the downstream end of the reactor. The gases are sampled into a 10 cm long infrared absorption cell. Product yields are then determined by infrared absorption measurements using a Nicolet Fourier transform infrared spectrometer. From comparisons of the observed infrared spectrum with previous calibrations, the concentrations of CO, CO₂, and CH₃OH are measured. In later experiments, the water cooled quench region was replaced with a heated zone in which the infrared cell and the gas lines leading to it were all heated to 70 C to test whether condensation of water vapor might be perturbing the experimental results.

High purity methane and oxygen are used as reactants. The pressure in the cell is measured with a capacitance manometer and the gas flows are measured and controlled using Tylan mass flow controllers. For experiments with laser initiation, a small amount of reagent grade acetone is premixed in a stainless steel tank with methane, so that the acetone concentration can be easily controlled by controlling the flow of the mix.

The photolysis laser is a Lumonics 860 rare gas-halide excimer laser operating on ArF at 193 nm. The typical fluence (energy/cm²) used in the experiments is 19 mJ/cm². The laser is operated at a repetition rate of 5 Hz.

Typical operating conditions are a temperature of 723 K, total pressure of 1650 torr, 9.95 % oxygen (164 torr), and flows of 0.2-1.1 standard liter/minute. Residence times in the cell are varied by changing the flow rates. In a series of experiments, typically 4 different residence times are measured and then one of these is repeated to verify that the results are reproducible. In the preliminary experiments described here, temperature uniformity in the reactor was not ideal and varied by as much as 25 degrees over the reaction region of interest.

RESULTS AND DISCUSSION

The initial experiments used simple thermal initiation of the reaction. A typical infrared spectrum of the products is shown in Figure 2. Although the spectrum is dominated by the methane and water absorption, the absorption bands of the CO, CH₃OH, and CO₂ are distinctive and do not appear to be overlapped with the bands of any other reactants or products.

Using thermal initiation of a 10 % mix of oxygen in methane at a total pressure of 1650 torr at 450 C, the major carbon-containing reaction product detected is CO. Significant amounts of methanol and of CO₂ are also produced. The amount of CO, CH₃OH, and CO₂ produced as a function of residence time in the cell are plotted in Figure 3

Experiments in which the infrared cell and collection line were kept at 70 C produced the same results as when the water cooled quenching region was used. This result would appear to rule out effects due to condensation of water and subsequent solubility of methanol in the water. The maximum amount of water produced in the reaction should be less than the vapor pressure of water at 70 C. To assess the effect of secondary oxidation of methanol produced in the reaction, small amounts of methanol were injected with the methane. For residence times of 12 seconds, the resulting methanol analyzed by infrared absorption was 80 % of the injected methanol. The production of CO and CO₂ was unaffected by the injection of methanol. At the longer residence time of 48 seconds, where most of the oxygen is consumed, 62 % of the methanol survived. In that case, it is assumed that the methanol measured is the sum of the methanol produced in the chain reaction plus the methanol injected. These results would seem to indicate that simple oxidation of methanol in the reactor does not dramatically lower the methanol yield.

For the laser initiation experiment experiments, the 193 nm photolysis of acetone using the short pulsed output of an ArF excimer laser was used as the prompt source of methyl radicals. The absorption cross section of acetone at 193 nm is relatively large ($3.6 \times 10^{-18} \text{ cm}^2$, measured using a commercial Cary 17 ultraviolet spectrometer). Methyl radicals and carbon monoxide have been identified as the major

photofragments of acetone photolysis at 193 nm.¹⁴ Using the same conditions of 1650 torr total pressure and 10 % oxygen, 0.7 torr of acetone was added to the gas flow and photolyzed using the repetitive output of the ArF laser. At the laser fluences used, approximately 7 % of the acetone was photolyzed per laser shot. Runs were made sequentially at various residence times in which first a run was made and analyzed with no photolysis laser and then a second run was made in which the photolysis laser was used.

By comparison with previous runs without acetone added, the addition of acetone appears to enhance the thermal initiation of the chain reaction, although the effect is relatively small. The effect of laser initiation is much more dramatic. Although only a small amount of acetone (less than 1 torr) has been added, a considerable amount of methanol and carbon monoxide have been produced using laser initiation, indicating that the laser photolysis of acetone is initiating the chain reaction. The results are shown in Figure 4 for the production of CO, CH₃OH, and CO₂. For the production of both CO and CH₃OH, significantly more product is produced using laser initiation than for thermal initiation at the same residence time. The production of CO₂ however is only slightly effected when the form of initiation is changed. This is illustrated in Figure 5 where the infrared spectra of methanol and CO₂ are shown for both thermal and laser initiation. While the methanol has been greatly enhanced, the

CO₂ has not changed much. The CO₂ produced appears to be more a function of residence time in the cell than sensitive to the initiation of the chain reaction. This is an encouraging result, since presumably by using unconventional initiation, the residence time in the cell can be shortened and the secondary chemistry minimized, resulting in better yields of desirable products.

One goal of this project has been to find a viable means of converting methane into methanol. The preliminary results shown above indicate that under conditions of relatively high oxygen/methane ratios, CO is the dominant product. A key question is to address is whether reducing the oxygen/methane ratio should improve this product yield to favor the production of methanol. As discussed earlier, the time scale for the production of significant amounts of product is a function of the initiation step and of the rate limiting steps in the chain reaction. The product yields, however, are more a function of competitive channels in the chemistry of particular radicals in the chain reaction.

In the case of the partial oxidation of methane to produce methanol, the fate of the methoxy radical is particularly important. Reaction 5, the reaction of methoxy with methane, is the source of production of methanol, while reactions 6 and 7 are the primary competitive removal steps for methoxy radical. In this system at 450 C, formaldehyde

produced by these reactions presumably decomposes to form the CO observed experimentally. The observation that production of both CO and CH₃OH are enhanced by laser initiation suggests that both are produced as a result of the chain reaction. For higher relative methanol yields (compared to CO), the oxygen/methane ratio must be lowered to minimize the deleterious effect of reaction 6.

Using the reaction constants recommended by Tsang and Hampson⁵, the relative methanol yields can be calculated as a function of oxygen/methane ratio and temperature. Using as rates, $k_5 = 2.6 \times 10^{-13} \exp(-4450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_6 = 1.1 \times 10^{-13} \exp(-1310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_7 = 5.1 \times 10^{12} T^{-6.12} \exp(-16660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and assuming no losses by collisions with the wall, a constant oxygen/methane ratio, no additional methoxy consuming reactions (other than reactions 5, 6, and 7), and no subsequent chemistry of methanol produced, the relative methanol/[CO, CH₂O] yield can be calculated analytically and is given by

$$\begin{aligned} \text{Relative CH}_3\text{OH Yield} &= \frac{k_5(T)[\text{CH}_4]}{k_5(T)[\text{CH}_4] + k_7(T)[\text{CH}_4] + k_6(T)[\text{O}_2]} \\ &= \frac{k_5(T)}{k_5(T) + k_7(T) + k_6(T)[\text{O}_2]/[\text{CH}_4]} \end{aligned}$$

From this expression, the relative methanol yield is a function of the oxygen/methane ratio and temperature but is not dependent on the total pressure. The results of this expression are displayed graphically in Figure 6. Clearly, a reduced oxygen/methane ratio leads to a higher relative methanol yield. Figure 6 also indicates that the relative product yield is better at temperatures lower than 450 C and that there is an optimum temperature for the best relative yield. At low temperatures, the methoxy chemistry is dominated by reactions with oxygen while at very high temperatures, the thermal decomposition of methoxy is very important. At intermediate temperatures and low oxygen/methane ratios, the reaction of methoxy radical with methane to produce methanol becomes the dominant removal reaction for methoxy. In principle, by initiating the chain reaction at lower temperatures using laser or other non-thermal techniques, it may be possible to better control the chemistry.

We should note that the rate constants $k_5(T)$ and $k_7(T)$ have not been measured experimentally and are estimates. The decomposition rate constant $k_7(T)$ has been estimated in an earlier study¹⁵ to be quite different from the value recommended by Tsang and Hampson⁵. In that case, while a low oxygen/methane ratio continues to be critical for a high relative methanol yield, the predicted temperature dependence

is much less dramatic. Clearly, it is important that these critical rate constants be evaluated experimentally.

The simple model shown above predicts a higher methanol yield than we observe experimentally. There may be several reasons for this. First, as discussed above, the rate constants $k_5(T)$ and $k_7(T)$ have not been measured experimentally and in their evaluation, Tsang and Hampson⁵ place uncertainties of factors of 3 and 4, respectively, on these two rate constants. That could account for much if not all of the discrepancy. Second, wall reactions are not accounted for in the present mechanism. This could lead to decomposition channels to produce CO not considered in the above discussion. In particular, under these conditions the methyl peroxy radical and methyl hydroperoxide are particularly long lived and wall reactions of these important species must be considered. Early experiments in which a stainless steel tube was used as the reaction vessel failed to produce any reaction under these same conditions of temperature and pressure. When a quartz liner was inserted in that early cell, the reaction was observed. This clearly indicates that wall collisions are important. While stainless steel is far worse than quartz, collisions with the quartz walls may still alter the chemistry even when the chain reaction proceeds. Third, at the flow rates used in these experiments back diffusion is not negligible and may play a role. In particular, this diffusion makes the definition of

residence time in the cell somewhat unclear. Fourth, the secondary chemistry of methanol may be important, although based on our experiments methanol appears to survive in the presence of oxygen under these conditions. Fifth, since the partial oxidation of methane is exothermic, a significant temperature rise could occur during the reaction. As shown in Figure 6, such a temperature rise would result in lowered methanol yields.

As discussed above, the temperature dependence of the relative methanol yield suggests that lower temperatures may be better. Future experiments must determine whether by varying the pressures, cell size, etc. it is possible to get chain reactions to occur rapidly enough at those temperatures to be important.

CONCLUSIONS

These experiments indicate that by using laser initiation the time scale necessary for the partial oxidation of methane by oxygen can be shortened. The product yields appear to be similar to those obtained in our apparatus under thermal-initiation conditions, as expected. Further experiments are in progress to investigate temperatures, pressures, and methane/oxygen ratios where thermal initiation is too slow to be practical. Under some of these conditions, it may be

possible to achieve product yields quite different from those that can be obtained by thermal initiation. Experiments are also in progress to measure the reaction rate constants of the important steps in this partial oxidation and to model the reaction using kinetic codes.

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FIGURE CAPTIONS

Fig. 1. Schematic of experimental apparatus for the study of both thermal-initiated and laser-initiated partial oxidation of methane by oxygen.

Fig. 2. FTIR spectrum of the methane/oxygen gas mixture following reaction at 450 C.

Fig. 3. Amounts of CH_3OH , CO , and CO_2 produced by thermal initiation at several different residence times in the cell at 450 C, total pressure of 1650 torr, and 10 % oxygen.

Fig. 4. Amounts of CH_3OH , CO , and CO_2 produced by both laser initiation and thermal initiation when 0.7 torr of acetone is added to the 1650 torr mix of 10 % O_2/CH_4 at 450 C at two different residence times.

Fig. 5. Infrared spectra showing the effect of laser initiation compared to thermal initiation when 0.7 torr of acetone is added to the methane/oxygen mix at 450 C.

Fig. 6. Relative methanol yields predicted from methoxy radical rate constants plotted as a function of temperature as several different oxygen/methane ratios.

SCHEMATIC OF EXPERIMENTAL APPARATUS FOR CH₃OH PRODUCTION BY THERMAL OR LASER INITIATION

REACTION PRODUCTS IDENTIFIED BY FTIR SPECTROSCOPY

AMOUNT OF PRODUCTS PRODUCED BY THERMAL
 DECOMPOSITION OF CH₄ AS A FUNCTION OF
 RESIDENCE TIME
~~DATE: 11-1-68~~ ~~TIME: 11:00~~

FIGURE

STEVEN T. BROWN
 CHM-4
 - 6838

EFF. % OF INITIAL LIQUIDS COMPARED TO
THERMAL LIQUIDS OF A CH_4/O_2 ICE-OUT MIX

~~DATAFILE - THERM~~

STANDARD
CHOICE OF
SHADING

SPEN DACHEN
CAM-4
7-6878

**SIGNIFICANT ENHANCEMENT IN CH₃OH YIELD
PRODUCED BY LASER INITIATION
BUT NO CHANGE IN CO₂ YIELD**

A line graph showing the relative methanol yield as a function of temperature (T in Kelvin) for different oxygen-to-methane (O_2/CH_4) ratios. The y-axis is labeled 'RELATIVE METHANOL YIELD (%)' and ranges from 0 to 0.9. The x-axis is labeled 'T(K)' and ranges from 300 to 900. There are seven curves, each labeled with its corresponding O_2/CH_4 ratio: 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, and 0.10. The curves show a peak yield that shifts to higher temperatures and decreases in magnitude as the O_2/CH_4 ratio increases. The peak for the 0.001 ratio is at approximately 550 K with a yield of about 0.84. The peak for the 0.10 ratio is at approximately 650 K with a yield of about 0.15.

T(K)	0.001	0.002	0.005	0.01	0.02	0.05	0.10
300	0.00	0.00	0.00	0.00	0.00	0.00	0.00
400	0.50	0.25	0.10	0.05	0.02	0.01	0.00
500	0.80	0.65	0.45	0.25	0.15	0.08	0.03
550	0.84	0.75	0.55	0.35	0.22	0.12	0.05
600	0.75	0.65	0.60	0.45	0.32	0.18	0.10
650	0.55	0.45	0.45	0.40	0.35	0.22	0.15
700	0.35	0.30	0.35	0.30	0.25	0.18	0.12
800	0.10	0.08	0.10	0.08	0.06	0.04	0.02
900	0.05	0.04	0.05	0.04	0.03	0.02	0.01