

## Partial Oxidation of Methane by Laser-initiated Chain Reaction

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Using  $N_2O$  as a source of  $O(^1D)$  by ArF excimer laser irradiation, an experimental work on partial oxidation of methane was performed at 200-350 °C and 300 or 600 Torr to find out methanol and several oxygen containing compounds with some  $C_2$ - $C_3$  hydrocarbons as products. Methane conversion and methanol selectivity increased in the presence of  $O_2$ , indicating that a chain reaction was significantly promoted.

In recent years, several attempts to use lasers in synthetic chemistry have been reported, the high power of which with high monochromaticity can induce a specific excitation of molecules either electronically or vibrationally to initiate chemical reactions or change their course. In the synthesis of vinyl chloride<sup>1)</sup> and high pressure polymerization of ethylene,<sup>2)</sup> for example, long chain reactions have been successfully induced by the excimer laser irradiation. Concerning the partial oxidation of methane, Murahara and Toyoda<sup>3)</sup> reported the formation of some amount of methanol from methane- $O_2$  mixtures according to the mechanism of two-photon absorption of  $F_2$  or ArF excimer laser light by methane, but only qualitatively. Baughcum et al.<sup>4)</sup> found that methanol was produced by the ArF excimer laser irradiation of methane- $O_2$  mixture containing a trace amount of acetone, but the yield of methanol was only about 2.5% of the main product CO. Total product analysis was not given in both of the above papers.<sup>3),4)</sup>

The object of the present work is to investigate in more details the effect of ArF excimer laser radiation to a system of methane and  $O_2$  containing  $N_2O$  at moderate temperatures, intending to attain a high quantum yield and selective methanol synthesis. It was found that the product distribution of not only oxygen-containing compounds but also hydrocarbons varied significantly depending on the progress of subsequent chain propagation steps initiated by  $O(^1D)$  produced in the laser photolysis of  $N_2O$ .

The experimental apparatus consisted of a pulsed laser, reaction cell, and gas chromatography. The cylindrical reaction cell (40 mm inner diam. x 12 cm) was made of quartz equipped with windows of Suprasil II at both ends, and surrounded by heating coils to elevate the temperature. Short ultraviolet laser pulses of ArF excimer laser (10 mJ or less/pulse, 193 nm) radiated at 10 Hz the reaction mixture for 60 min. The composition of the reactant gas was kept constant at  $CH_4/N_2O=2/1$  or  $CH_4/N_2O/O_2=4/2/1$ . Total cell pressure was 300 Torr or

600 Torr. Products were analyzed gas chromatographically, though a few possible products such as formaldehyde were not determined. The methane conversion was defined as the ratio of the sum of carbon containing products to the initial amount of methane. The excimer laser light was mainly absorbed by  $N_2O$ , but not by methane and  $O_2$ . The absorption coefficient of  $N_2O$  was found to be effectively independent of the temperature in the present experiments, and about 90% of the irradiated light was absorbed within the cell length of 12 cm.

Since no product was obtained under the same reaction condition without laser irradiation, the initial elementary reaction with laser irradiation is considered to be the production of  $O(^1D)$  atoms in the  $N_2O$  photolysis. With laser irradiation, hydrocarbons such as ethane and propane, methanol, ethanol and small amount of other oxygenates such as dimethyl ether, acetaldehyde and methyl formate were formed. Tables 1 and 2 show the product selectivities in the absence or presence of  $O_2$ , respectively. In the absence of  $O_2$  (Table 1), the selectivity for ethane is very high while those of CO and  $CO_2$  are rather low, and

Table 1. Product Selectivity in the Absence of Oxygen

Press. Torr <sup>a)</sup>	Temp °C	CH <sub>4</sub> Conv. %	Selectivity /%									
			CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> O	CH <sub>3</sub> CHO	HCOOCH <sub>3</sub>
300	200	7.6	24.4	2.7	1.3	54.3	4.3	6.3	3.3	1.0	2.3	0.0
	250	7.9	22.1	2.0	1.5	57.9	4.9	5.2	3.7	0.7	2.0	0.0
	300	11.6	29.2	2.9	1.2	51.9	6.6	3.1	3.5	0.3	1.0	0.0
	350	17.8	34.7	4.8	1.2	42.3	8.6	1.0	2.9	0.0	0.5	3.6
600	200	5.2	18.4	2.3	1.5	57.2	3.7	8.8	3.9	1.4	2.7	0.0
	250	4.9	16.0	1.7	1.7	61.3	3.9	7.2	4.3	1.0	2.9	0.0
	300	5.0	20.4	2.1	1.8	57.9	3.6	7.4	4.2	0.6	1.8	0.0
	350	9.0	24.8	3.7	1.3	53.1	6.0	2.9	3.6	0.2	0.9	3.4

a) 1 Torr = 133.32 Pa.

Table 2. Product Selectivity in the Presence of Oxygen

Press. Torr <sup>a)</sup>	Temp °C	CH <sub>4</sub> Conv. %	O <sub>2</sub> Conv. %	Selectivity /%									
				CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> O	CH <sub>3</sub> CHO	HCOOCH <sub>3</sub>
300	200	14.7	75.6	69.1	15.4	0.0	0.9	0.0	12.9	0.0	0.3	0.0	0.0
	250	22.3	100	71.4	17.6	0.1	5.6	0.2	2.5	0.5	0.2	0.4	1.5
	300	25.7	100	66.5	17.4	0.1	10.3	0.9	2.4	0.8	0.2	0.3	1.0
	350	31.1	100	55.3	16.7	0.4	17.7	3.8	0.8	1.2	0.1	0.3	3.1
600	200	7.5	33.6	70.6	9.1	0.0	1.2	0.0	14.4	0.0	0.4	0.0	0.0
	250	15.4	85.6	76.9	16.2	0.0	1.3	0.0	4.2	0.0	0.1	0.1	0.0
	300	19.6	100	69.5	18.6	0.1	3.4	0.0	7.4	0.3	0.3	0.3	0.1
	350	24.1	100	64.9	17.1	0.1	10.3	0.8	5.0	1.0	0.3	0.3	0.2

a) 1 Torr = 133.32 Pa.

the methane conversion is relatively low. In the presence of  $O_2$  (Table 2), the selectivities for CO and  $CO_2$  are relatively high, and methanol yield is also higher. Not only CO and  $CO_2$  but also methanol are produced mainly by the chain reaction wherein involved are the oxygen molecules, taking into account that insertion products of  $O(^1D)$  for methane,  $(CH_3OH)^*$ , cannot be stabilized under such low pressure conditions, as suggested by Lin and DeMore,<sup>5)</sup> and Kajimoto et al.<sup>6)</sup>

Figure 1 shows the methane conversion as a function of temperature under the pressures of 300 and 600 Torr, which increases with increasing the reaction temperature. Figure 2 shows the temperature dependence of the ratio of methane consumption to  $N_2O$  consumption as a measure of the chain length. The ratio is much larger in the presence of  $O_2$  than that in its absence, and it seems to increase with increasing the reaction temperature, which suggests that the chain reaction contains an elementary reaction possessing some activation energy. Though the chain length tends to decrease in higher temperature range, it is possibly due to the complete consumption of  $O_2$  during the irradiation. On the other hand, Table 2 indicates that the higher temperature and lower pressure are favorable as far as the selectivity for hydrocarbon products are concerned, whereas the lower temperature and higher pressure are favorable for methanol formation. Therefore careful selection of reaction conditions, in view of controlling the key elementary reactions, must be made for achievement of higher chain length and

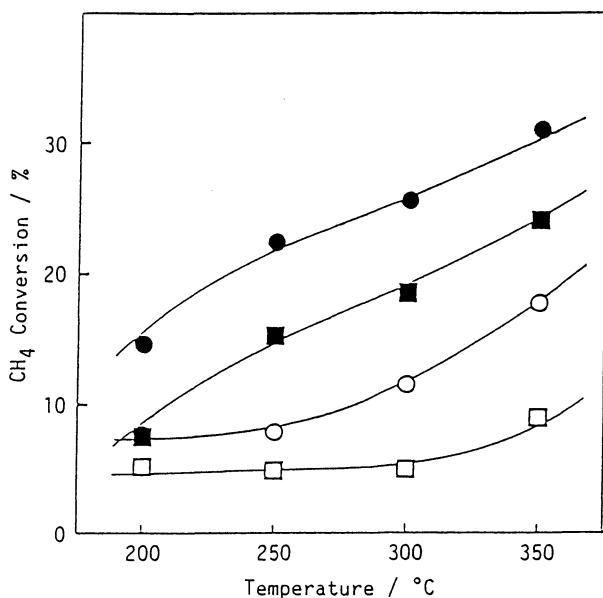


Fig. 1. Conversion of  $CH_4$  as a Function of Temperature.  $CH_4/N_2O/O_2 = 4/2/1$  at total pressure 300 Torr (●) and 600 Torr (■).  $CH_4/N_2O = 2/1$  at total pressure 300 Torr (○) and 600 Torr (□).

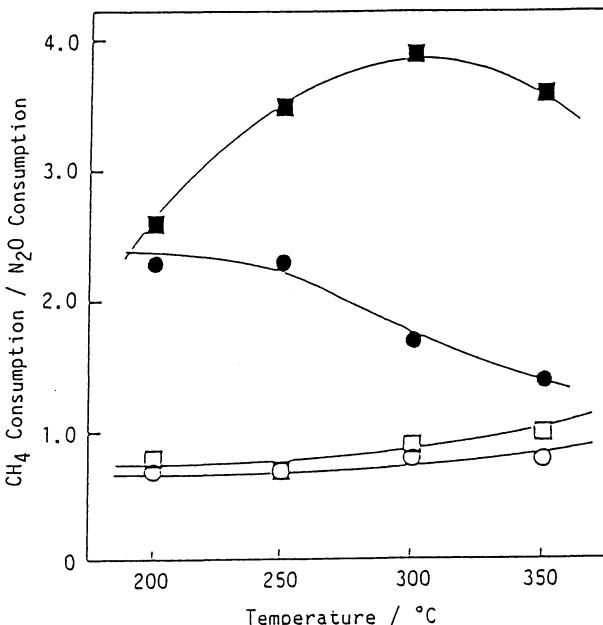
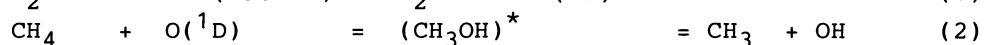


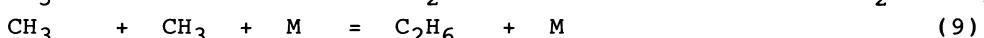
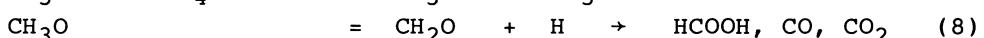
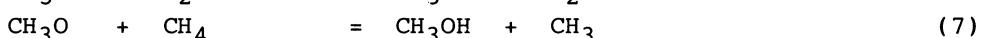
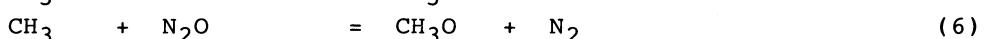
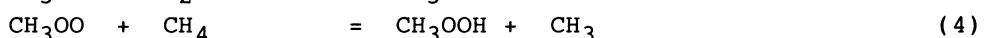
Fig. 2. Chain Length.  $CH_4/N_2O/O_2 = 4/2/1$  at total pressure 300 Torr (●) and 600 Torr (■).  $CH_4/N_2O = 2/1$  at total pressure 300 Torr (○) and 600 Torr (□).

higher methanol selectivity.

From these experimental results, the initial reaction steps can be explained as follows;



The activation energy of reaction 2 is expected to be quite low.<sup>7)</sup> The subsequent reaction progress may be different depending on whether O<sub>2</sub> is present or absent. In the absence of O<sub>2</sub>, methyl radicals react with N<sub>2</sub>O to form methoxy radicals (reaction 6) at a relatively low rate, or recombine to form ethane (reaction 9). In the presence of O<sub>2</sub>, on the other hand, methyl radicals produced through reaction 2 would react with O<sub>2</sub> to form methylperoxide (reaction 3), and the following reactions 4, 5, and 7 may determine the chain length and the product selectivity.



The experimental attempts as well as simulation works to attain higher quantum yield and higher methanol selectivity in this reaction system are in progress, varying extensively the reaction conditions such as temperature, pressure and intensity of laser radiation.

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