

Conversion of  $\text{CH}_4$  into  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  by the Chlorine-Catalyzed Oxidative-Pyrolysis (CCOP) process: I. Oxidative Pyrolysis of  $\text{CH}_3\text{Cl}$

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INTRODUCTION:

Methane is available in large quantities in natural gas, thus constitutes an important raw material for the synthesis of higher molecular weight hydrocarbons. Processes exist to convert methane into acetylene, ethylene, and hydrogen using high temperature pyrolysis. However, at the high temperatures needed for the thermal decomposition of methane, the yields of more valuable liquid and gaseous products are too low due to the formation of excessive amounts of carbonaceous solids (see (1) and references therein).

In an earlier patent Gorin (2) proposed a chlorine-catalyzed process in which methane conversion was achieved via  $\text{CH}_4$  chlorination, followed by the pyrolysis of chlorinated methanes (CM) and formation of  $\text{C}_2+$  products and  $\text{HCl}$ . The  $\text{HCl}$  produced can either be converted into chlorine via the well-known Deacon reaction, or can be used to convert  $\text{CH}_4$  into  $\text{CH}_3\text{Cl}$  via oxychlorination process, thus completing the catalytic cycle for chlorine. Recently, Benson (3) patented a process similar to that of Gorin (2), in which the flame reactions of  $\text{Cl}_2$  and  $\text{CH}_4$  were involved. Later, Weissman and Benson (4) studied the kinetics of  $\text{CH}_3\text{Cl}$  pyrolysis.

As expected from bond dissociation energy considerations, the decomposition temperatures for CM would be lower than that for methane, thus the destruction of valuable pyrolysis products, which include acetylene and ethylene would be suppressed. However, in spite of the lower temperatures required for CM pyrolysis, the formation of carbonaceous solids still is a problem (2,4), and this renders the direct pyrolysis of CMs unattractive for practical applications.

The Chlorine-Catalyzed Oxidative-Pyrolysis (CCOP) process developed ameliorates the problem of formation of solid products, while maintaining high yields for acetylene and ethylene (5,6). The CCOP process exploits the high-temperature, non-flame reactions of methane, chlorine, and oxygen, and forms an important bridge between combustion chemistry, halogen inhibition processes (7,8) and chemical reaction engineering. Although some carbon monoxide forms in the CCOP process, CO is a gaseous product thus can be handled easily. In addition, CO can itself be used to synthesize higher molecular hydrocarbons as well.

EXPERIMENTAL:

The experiments were conducted in a 2.1 cm ID quartz tube which was about 100 cm long, and was placed in a 3-zone Lindbergh furnace. A small amount of  $\text{CH}_3\text{Cl}/\text{O}_2$  mixture was injected directly into pre-heated argon carrier gas. Experiments were reasonably isothermal as determined by thermocouples. Although laminar flow conditions were present, the deviation

from ideal plug flow behavior was determined to be in the range 10-15%, by the measurements of the concentration profiles in the radial direction.

Species profiles were determined by withdrawing gases through a water-cooled quartz sampling probe positioned centrally at the downstream of the reaction zone, followed by gas analysis by on-line mass spectrometry.

#### RESULTS AND DISCUSSION:

The experimental conditions investigated are presented in Table I. It should be noted that under these conditions, homogeneous gas-phase kinetics would dominate the reaction processes, with minor contributions from surface induced reactions (4,9).

TABLE I  
Experimental Conditions Investigated.  
T=980C, P=515 Torr, v=150 cm/s, res. time=50-250 ms

Species	Mixture A		Mixture B
	Mole percent		Mole percent
	CCOP	Process	St. Pyrolysis
CH <sub>3</sub> Cl	7.32		7.47
O <sub>2</sub>	2.05		-
Ar	90.6		92.5

It was possible to conduct experiments with Mixture A indefinitely without any visible signs of formation of solid deposits at the exit of the transparent quartz reactor. Use of mixture B, however, immediately resulted in the formation of dark solid deposits, which rendered the quartz reactor opaque. The formation of solid deposits in the absence of oxygen, however, is an expected result, consistent with the findings of previous investigators (2,4).

In all the experiments the major species quantified, other than the reactants and argon, were: C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>3</sub>Cl, CH<sub>4</sub>, HCl, and CO. Minor species identified, but not quantified were: C<sub>6</sub>H<sub>6</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and HCHO.

In Figure 1 the mole percent profile for CH<sub>3</sub>Cl and temperature are presented as a function of axial position. In addition, the percent for unaccounted carbon (UC) is also presented. UC is defined as the percent of carbon unaccounted for by the measurements of major gaseous species; thus it represents a measure of extent of formation of solid products.

As seen from the UC profiles in Fig 1, the formation of high molecular weight products, which cannot be quantified by mass spectrometry, is indeed a problem in the absence of O<sub>2</sub>. This result is consistent with our qualitative observations noted earlier and the results of Gorin (2), and Weissman and Benson (4).

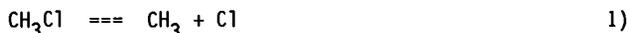
In Figure 2 the mole percent profiles for HCl, O<sub>2</sub>, and CO are presented. The HCl mole percents were calculated from chlorine atom balances, from the measurements of the overall conversion of CH<sub>3</sub>Cl, and by assuming that no chlorine is associated with UC. The conversion of O<sub>2</sub> was quite low,

less than about 10%, consistent with the formation of low levels of CO, and by the absence of quantifiable amounts of CO<sub>2</sub> or H<sub>2</sub>O.

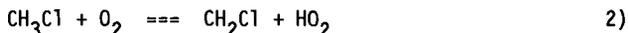
In Figure 3 the profiles for H<sub>2</sub> and CH<sub>4</sub> are presented. The mole fractions for H<sub>2</sub> were obtained from hydrogen atom balances. In Figure 4 the profiles for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>3</sub>Cl are shown. These profiles suggest the eventual establishment of pseudo-stationary values for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at higher CH<sub>3</sub>Cl conversions, consistent with the non-chain character of the process. As seen from these profiles, the levels of these products were not sensitive to O<sub>2</sub>.

#### REACTION MECHANISM:

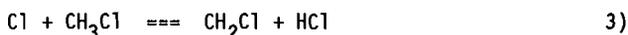
Detailed chemical modeling of the CCOP process suggests that CM pyrolysis starts with the well known initiation step (10):



as well by the following route in the presence of O<sub>2</sub>:



These reactions are followed by:

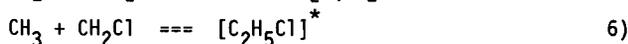
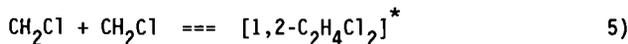


Once formed, HCl undergoes the following fast reaction:



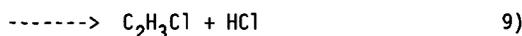
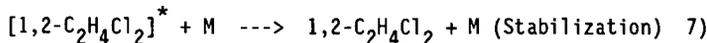
regenerating Cl, and forming CH<sub>4</sub> as an inevitable by-product of CM pyrolysis. Reaction 4 also rapidly consumes the CH<sub>3</sub>, therefore rendering CH<sub>2</sub>Cl as the most important C<sub>1</sub> radical in the system.

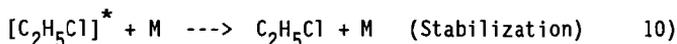
The chemically activated recombination of CH<sub>2</sub>Cl, as well as CH<sub>2</sub>Cl and CH<sub>3</sub> then determine the major product distributions in the CCOP process. These reactions are the following:



where [ ]\* denotes the chemically activated adduct. The CH<sub>3</sub>+CH<sub>3</sub>=[C<sub>2</sub>H<sub>6</sub>]\* reaction is unimportant because of the lower concentrations of the CH<sub>3</sub> radicals.

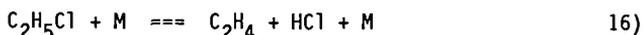
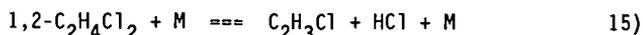
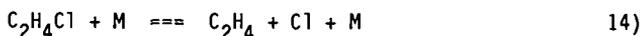
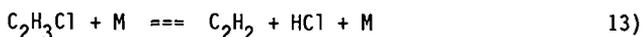
The energized adducts [1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>]\*, and [C<sub>2</sub>H<sub>5</sub>Cl]\* then undergo the following parallel stabilization and decomposition reactions:





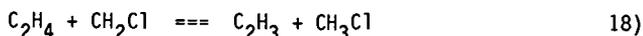
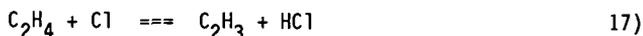
As apparent from these reactions gas density (M) has a significant impact on the nature of the ultimate product distribution. For example, at higher pressures and/or lower temperatures where M is high, collisional stabilization of the chemically activated intermediates is enhanced, thus the formation of recombination products would be favored. Conversely, at low pressures and/or higher temperatures where M is low, HCl and Cl elimination channels would gain greater significance.

These radical combination reactions are then followed by the following, again pressure-dependent, unimolecular reactions leading to the formation of  $C_2H_2$ , and  $C_2H_4$ :



Reaction 13 is the major channel for the formation of  $C_2H_2$  and for the destruction of  $C_2H_3Cl$ . The formation of  $C_2H_4$  occurs primarily via reaction 11, and to a lesser extent by reactions 14, and 16.

Ethylene also undergoes the following destruction processes:

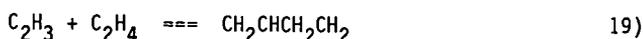


and form one of the most important  $C_2$  radicals in the system,  $C_2H_3$ . Similar destruction channels for  $C_2H_2$  would be too slow to be of any significance.

In the absence of oxygen, the primary reaction pathways available for  $C_2H_3$  are its polymerization:



and to a lesser extent:



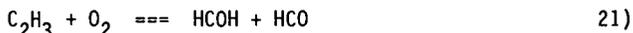
or its highly-endothermic, thus slow decomposition to acetylene:



The  $CH_2CHCH_2CH_2$  and  $CH_2CHCHCH$  radicals subsequently undergo dehydrogenation, hydrogenation, further addition reactions with  $C_2H_2$  and  $C_2H_4$ , cyclize and ultimately result in the formation of high molecular weight

carbonaceous solids. Although the detailed chemical kinetic steps leading to the formation of solid products are not fully known at present, the process nevertheless is well known to be extremely rapid (11), and reaction 18 is believed to play a pivotal role (4,12, 13).

In the presence of oxygen, however, the  $C_2H_3$  radical has an additional fast reaction channel which effectively competes with the above processes:



This elementary reaction have only recently been isolated and studied (14), and was shown to have no activation energy barrier. Consequently, oxygen has a profound influence on the processes of formation of high molecular weight hydrocarbon solids and carbon by directly intercepting the  $C_2H_3$  radicals. The HCOH and HCO formed by reaction 21 subsequently are converted into CO.

As evident from the above reaction mechanism, although  $O_2$  interrupts the processes that ultimately lead to the formation of solid deposits, it does not directly interfere with the reactions responsible for the formation of ethylene and acetylene. This is supported by the experimental measurements presented in Figure 4, in which the mole percents for  $C_2H_2$  and  $C_2H_4$  remained nearly the same both in the presence and absence of oxygen at the same extent of conversion of  $CH_3Cl$ .

It is most important to note that the success of the CCOP process depends on the presence of the following combustion inhibition reaction, which also is the major route for  $H_2$  formation:



Reaction 22, because of its lower activation energy, efficiently removes the H radicals from the system, and renders the following important combustion chain branching reaction:



ineffective in building up the concentrations of O and OH radicals (7,8). Consequently the formation of flames, thus the destruction of CM and valuable products are prevented.

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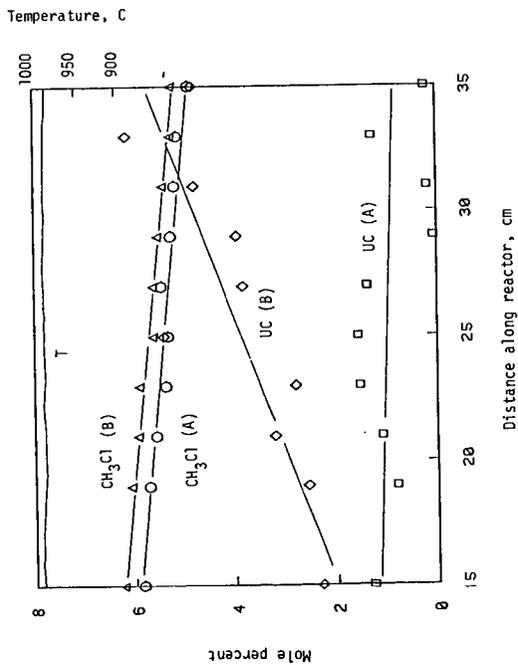


Figure 1. Profiles for  $\text{CH}_3\text{Cl}$ , UC and Temperature.

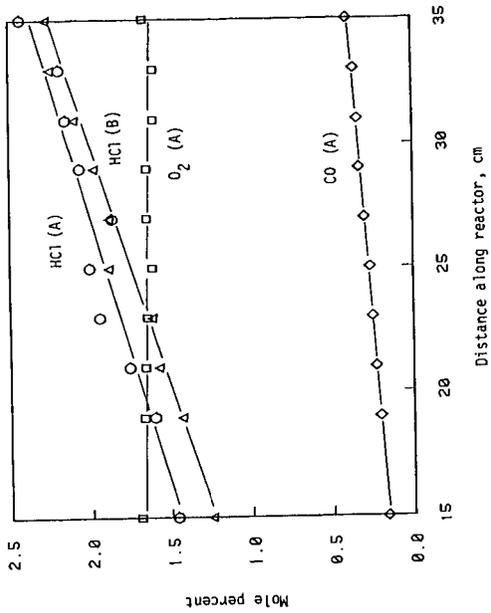


Figure 2. Profiles for HCl,  $\text{O}_2$ , CO.

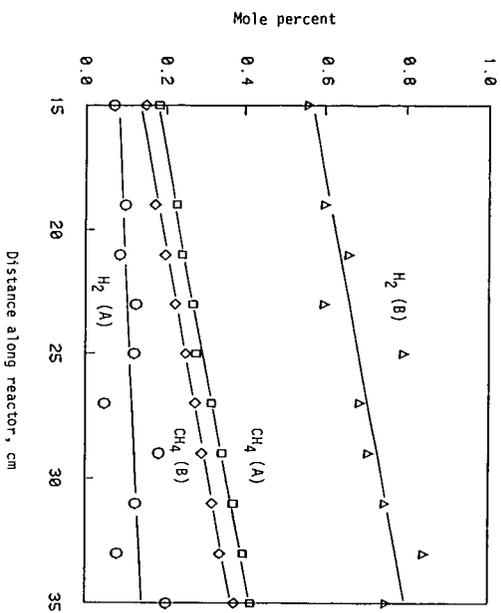


Figure 3. Profiles for H<sub>2</sub> and CH<sub>4</sub>.

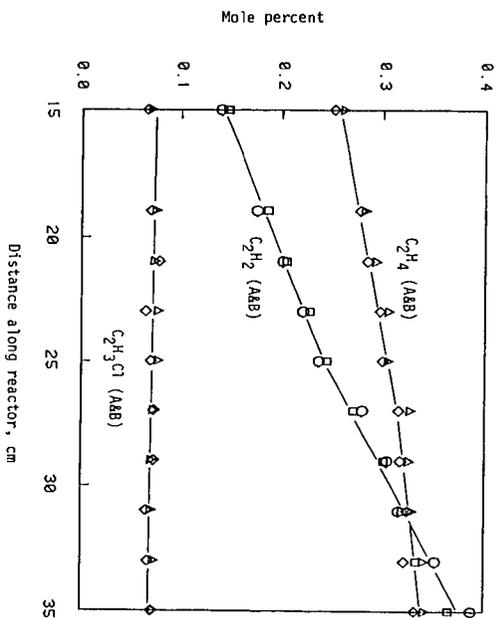


Figure 4. Profiles for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>3</sub>Cl.