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Conversion of Methane into Ethylene, Acetylene and Ethane by the CCOP
Process: Control of Product Selectivities

by

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ABSTRACT:

The oxidative pyrolysis of CH_3Cl , representing the second stage in the Chlorine-Catalyzed Oxidative-Pyrolytic (CCOP) conversion of methane into C_2 hydrocarbons have been studied in the presence of CH_4 in a flow reactor operating at 0.7 atm and 900-950 C. The effects of temperature, mixture composition, in particular the concentration of O_2 , and residence times on CH_3Cl conversion and selectivity towards the formation of C_2 products have been explored experimentally. The role of CH_4 and other operational variables in effecting rates and selectivities will be discussed in view of our current understanding of the detailed chemical kinetic aspects of the CCOP process.

INTRODUCTION:

Chlorine-Catalyzed Oxidative-Pyrolysis (CCOP) process was recently developed as a practical method to convert methane, the major component in natural gas, into more valuable products such as acetylene and ethylene (Senkan 1987a). In the CCOP process CH_4 is chlorinated to form chlorinated methanes (CM) first, followed by the oxidative pyrolysis of CM to form C_2 products such as C_2H_4 , C_2H_2 , C_2H_6 , $\text{C}_2\text{H}_3\text{Cl}$, synthesis gas (CO and H_2), and HCl in the second step. The process developed ameliorates the problem of formation of carbonaceous solid deposits inherent with the earlier chlorine-catalyzed methane conversion processes which took place in the absence of oxygen (Gorin 1943, Benson 1980, Weissman and Benson 1984). The HCl produced can either be converted back to chlorine via the well-known Deacon reaction and recycled, or can be used to oxychlorinate methane to form CMs, thus completing the catalytic cycle for

chlorine (Senkan 1987b).

In previous studies we reported experimental product distributions for the oxidative pyrolysis of isolated CH_3Cl in the presence of an inert (argon) carrier gas (Granada et al. 1987). In parallel, a detailed chemical kinetic mechanism for the oxidative pyrolysis of CH_3Cl was also developed and validated (Karra and Senkan 1988a).

As discussed in these earlier studies the selectivity for C_2H_4 can be substantially high, e.g. about 40%, at low conversions of CH_3Cl . However, it decreases rapidly with increasing conversion, rendering acetylene as the major product beyond 30% conversion of CH_3Cl . Since C_2H_4 is a more desirable product, the identification of proper process conditions that will favor its formation clearly are of interest (C&E News 1987).

Pyrolysis of CH_3Cl in the presence of CH_4 increases C_2H_4 production over C_2H_2 as demonstrated by Weissman and Benson 1984. However, in the absence of O_2 , the process also leads to the formation of significant levels of carbonaceous deposits, in particular coke, which is undesirable.

In this communication we present results on the oxidative pyrolysis of CH_3Cl conducted in the presence of CH_4 , in which coke formation is avoided. The effects of temperature, O_2 concentration and residence times on the conversion of CH_3Cl and product distributions are discussed based on experiments conducted at 0.7 atm, 900-950 C, and for a $\text{CH}_3\text{Cl}/\text{CH}_4$ ratio of about 0.25. In addition, the role of these process variables on conversion and selectivity is discussed based on our current understanding of the detailed chemical kinetic aspects of the CCO process.

EXPERIMENTAL:

The experimental facility used has been discussed in detail previously (Granada et al. 1987), thus only a brief summary will be presented here. The

experiments were conducted in a 2.1 cm ID quartz tube which was placed in a 3-zone Lindbergh furnace. The first zone of the furnace, which is about 15 cm long, was used to preheat methane which served as a reactive carrier gas. Mixtures of $\text{CH}_3\text{Cl}/\text{O}_2$ were then introduced into pre-heated methane using an air-cooled probe through radially directed injection holes. Small amounts of nitrogen (3-5%) also were introduced into the feed mixture as an internal reference gas.

Gases used were acquired either from the Matheson Co. (Joliet, IL) or from Bennet Welding Supply Co. (Bensenville, IL), and had the following reported purities: CH_3Cl :99.5% as liquid, CH_4 :99.97%, O_2 :99.6% extra dry, and N_2 :99.99%. They were used directly from the cylinders, and their flow rates were controlled by the combined use of two-stage regulators, rotameters and needle valves. The needle valves were maintained under critical flow conditions to establish uncoupled flow rates. A mechanical vacuum pump was then used to remove the reaction products from the system. The pressure in the reactor was kept slightly below atmospheric pressure (about 0.70 atm) in all the experiments to prevent toxic gases from leaking into the laboratory, and was monitored continuously by a capacitance transducer (MKS Baratron, Burlington MA).

Mean gas flow velocities in the reactor were in the range 1-10 m/s, suggesting that laminar flow conditions were present. However, the deviation from ideal plug flow behavior would be in the range 10-15%, the same order of magnitude as the other experimental errors (Cathonnet et al. 1981).

Gas samples were withdrawn continuously using a vacuum pump through a warm-water-cooled quartz sampling probe positioned centrally at the downstream end of the reactor, and then through a heated sample loop in the gas-chromatograph (Hewlett-Packard 5880A). The pressure in sampling lines and the loop was kept at about 0.25 atm to minimize the condensation of species, in particular H_2O and HCl . Following the establishment of steady sampling conditions, that were

determined in prior experiments by studying the variation of mixture composition as a function of sampling time, the sampling loop was automatically switched on-line with the helium carrier gas. Gas separation and detection were then accomplished by Porapak N (0.31 cm diameter by 1.8 m long) and by molecular sieve 5A (0.31 cm diameter by 1.8 m long) columns (both acquired from Alltech Assoc., Deerfield IL), and by the thermal conductivity detector, respectively.

Gas analysis was accomplished using standard gas chromatographic methods (GC). For reactants, i.e. CH_3Cl , CH_4 , O_2 , and N_2 , GC response factors were obtained directly by analyzing the reactor effluents in the absence of reaction, i.e. at low temperatures. For reaction products, such as C_2H_4 , C_2H_2 , C_2H_6 , $\text{C}_2\text{H}_3\text{Cl}$, and CO a certified calibration mixture (Matheson Co., Joliet IL) was used. For this calibration, a gas mixture having a composition reasonably close to those encountered in the experiments was acquired. Consequently, we estimate that the mole fractions obtained in this study should be accurate within $\pm 5\%$. Species mole fraction profiles were then obtained by moving the sampling probe relative to the stationary injection probe.

Carbon balances for each measurement were made by using the following definition:

$$\% \text{ Carbon balance} = \frac{(\text{gas-phase carbon}/\text{N}_2)_{\text{reaction mixture}}}{(\text{gas-phase carbon}/\text{N}_2)_{\text{feed mixture}}} * 100$$

and they were better than 95% for all the experiments.

RESULTS:

The major species quantified directly by GC were the reactants CH_3Cl , CH_4 , O_2 , and N_2 as the tracer gas, and the major carbon-containing products C_2H_4 , C_2H_2 , C_2H_6 and CO . Since only trace levels of CO_2 form in the CCOP process, it was neglected in the final product analysis. Unlike the oxidative pyrolysis of CH_3Cl , which leads to substantial $\text{C}_2\text{H}_3\text{Cl}$ formation, very little $\text{C}_2\text{H}_3\text{Cl}$ formed in

the current experiments when an excess CH_4 was present.

Before presenting any results a number of issues must be discussed concerning the experiments. First, as we noted previously even small amounts of O_2 in the mixture suppresses the extent of formation of carbon in the system, and this effect is most dramatic with regard to coke formation. On the other hand, when O_2 feed was deliberately cut off, rapid coking, manifested by the formation of black deposits on the inner surface of the reactor walls, was observed.

Second, although CH_4 actively participates in the process, and dramatically increases the concentration of C_2H_4 relative to C_2H_2 , the precise quantification of the extent by which CH_4 contributes to this phenomena was rendered difficult in the present studies because of CH_4 reformation from CH_3Cl and experimental errors. For example, the absolute concentrations of C_2 products formed in the experiments were of the same order of magnitude as the uncertainties in the measurements of CH_4 concentrations. Consequently, we report selectivities based on the amount of CH_3Cl reacted. This appears reasonable because CH_4 is expected to form as a major product in the oxidative pyrolysis of CH_3Cl even in the presence of excess methane based on detailed chemical kinetic calculations (Senkan 1988).

In order to systematically explore the effects of each of the process variables on CH_3Cl conversion and on product selectivities, we conducted experiments in which independently adjustable variables were changed one at a time. In Figure 1 the influence of temperature on carbon containing product concentrations in the CCOP process are illustrated for a mixture with the following pre-reaction composition: CH_3Cl 15.9%, CH_4 75.9%, O_2 4.12%, and N_2 3.98%. Nominal residence times were about 330 ms. In this and subsequent figures lines have been drawn through experimental data points (indicated by symbols) to indicate trends.

The compositions shown in this figure represent conditions at a fixed position near the exit of the reactor, and therefore do not precisely correspond to identical residence times. However, since the differences in temperatures between these experiments were at most 50 K, residence times are expected to be different by at most 5% due to temperature effects, well within normal experimental error limits. Product (carbon) selectivities, determined relative to CH_3Cl reacted, similarly are presented in Figure 2, together with the percent conversion of CH_3Cl .

As seen in Figure 1, temperature has the most dramatic effect on the concentration of CO, with CO mole percent increasing exponentially with reaction temperature. In contrast, the concentrations of all the C_2 products varied more gradually with temperature. These results can be explained in view of the detailed chemical kinetic mechanism for the CCOP process developed recently (Karra and Senkan 1988a), and will be discussed in a future publication (Senkan 1988).

The effects of O_2 concentration on rates and selectivities are presented in Figures 3 and 4, respectively. These results similarly were obtained by sampling gases near the exit of the reactor corresponding to a nominal residence time of about 330 ms. The reaction temperature was 920 C, and the following O_2 -free pre-reaction composition was used: CH_3Cl 20.6%, CH_4 74.8%, and N_2 4.56%. The concentration of O_2 in these experiments were changed by changing the flow rate of O_2 entering the reactor, while maintaining the flow rates of other gases constant. Consequently, the data points presented in Figures 3 and 4 also do not precisely correspond to same residence times. However, since O_2 represents at most 7% of the reaction mixture, differences in residence times are not expected to be different by more than this amount, again within experimental error limits. As evident from Figures 3 and 4, O_2 concentration directly effects the

level of CO formed in the system, while its impact on C₂ products is more subtle.

Since the CCOP process must proceed under non-flame conditions, the levels of O₂ in the mixture must be selected carefully (1987a). In this regard it is important to recognize that although the presence of some O₂ in the mixture is essential to prevent coke formation, an excess O₂ concentration is also undesirable because of the onset of flame reactions. The onset of flame reactions are characterized by the formation of excessive levels of CO, CO₂, H₂O and soot. The formation of excessive H₂O, in particular, causes operational problems because of its condensation together with HCl on cold surfaces at the exit of the reactor.

In Figures 5 and 6 the concentration and selectivity profiles along the reactor are presented for a mixture with the following pre-reaction composition: CH₃Cl 19.78%, CH₄ 71.62%, O₂ 4.23%, and N₂ 4.37%. These profiles were obtained at 920 C, and by moving the sampling probe along the reactor. The distance along the reactor was measured relative to the point of injection of the CH₃Cl/O₂ mixture into preheated CH₄. In this experiment, the total number of moles in the system remained essentially the same, i.e. the absolute concentration of N₂ measured by GC was constant, thus residence times were directly proportional to distance along the reactor. Since the mean gas velocity in the reactor was 1.15 m/s, the data presented in Figures 5 and 6 correspond to residence times ranging from 173 to 312 ms at the exit of the reactor.

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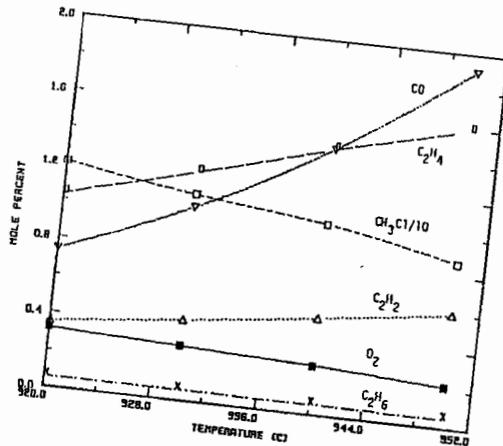


Figure 1. The effects of temperature on the concentration of species at a nominal residence time of 330 ms.

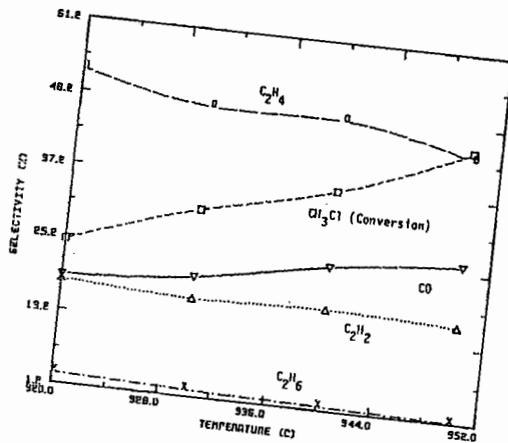


Figure 2. The effects of temperature on conversion and product selectivities at a nominal residence time of 330 ms.

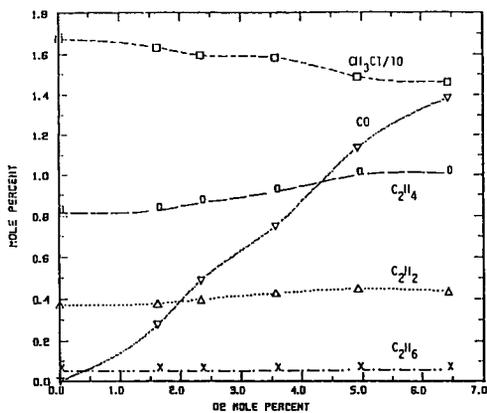


Figure 3. The effects of O₂ concentration on the concentration of species at 920 C and a nominal residence time of 330 ms.

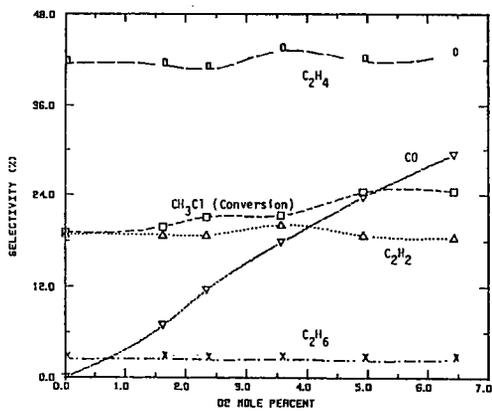


Figure 4. The effects of O₂ concentration on conversion and product selectivities at 920 C and a nominal residence time of 330 ms.

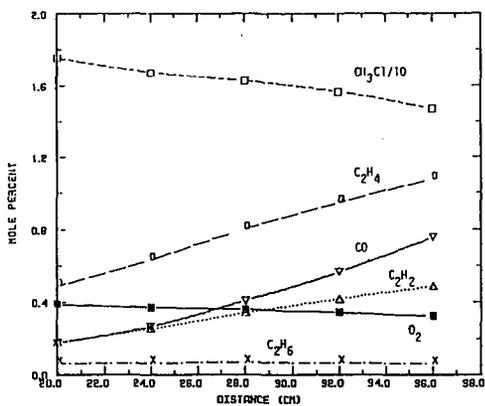


Figure 5. The effects of residence time on the concentration of species at 920 C.

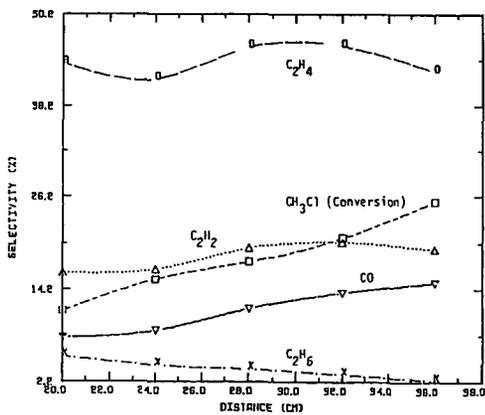


Figure 6. The effects of residence time on conversion and product selectivities at 920 C.