ABSTRACT

Title of Thesis: The oxidation of methylene chloride over manganese dioxide catalyst

Jun Du, Master of Science in Environment Science, 1990

Thesis directed by Professor Henry Shaw, Ph.D. of the Department of Chemical Engineering, Chemistry, and Environment Science.

This research presents results from a study with the goal of using a transition metal oxidation catalyst, manganese dioxide (MnO_2), to convert low concentrations of methylene chloride (CH_2Cl_2) in air and in a methane/air stream into CO_2, H_2O and HCl. Our objectives were to determine the oxidative effectiveness of the catalyst and its durability under the corrosive exposure to chlorine, HCl and other likely stack gas contaminants.

Experiments were carried out in a tubular packed bed integral reactor using gas chromatographic (FID and TCD) analysis for chlorocarbons and non-dispersive infrared analysis for CO and CO_2. The results indicate:

1. The light-off temperature for oxidation of the CH_2Cl_2/air mixture over MnO_2 is on the order of 500 K for space velocities from 1.67 to 6.67 v/v/sec.

2. There are two regions where rate is controlling: (i) in the range of 513-625 K, rate is controlled by kinetics, where higher temperatures increase conversion of CH_2Cl_2 and

selectivity to $CHCl_3$ and CCl_4, and (ii) above 675 K, the rate is controlled by bulk mass transfer, where the reaction rate is an insensitive function of temperature.

3. A typical material balance at 708 K shows that 100 ppm CH_2Cl_2 are converted to 8.4 ppm CO_2, 32.7 ppm $CHCl_3$, 9.2 ppm CCl_4, 3.7 ppm HCl (determined by titration), and 34.4 ppm CH_2Cl_2 come through unreacted.

4. The overall rate constant is:

$$k = 9{,}600\ (\pm 600)\ \mathrm{Exp}[-12.7(\pm 0.2)/RT] \text{ in } 1/\mathrm{sec}$$

where, activation energy is 12.7 kcal/mol and gas constant is 1.987 cal/(mol K).

5. Increased residence time changes selectivity from $CHCl_3$ to CCl_4.

6. Oxychlorination (the catalytic conversion of HCl to Cl_2 in the presence of O_2) apparently decreases the effectiveness of MnO_2 to produce CO_2 and HCl by forming $CHCl_3$ and CCl_4.

7. Since MnO_2 converts CH_2Cl_2 to higher chlorinated products rather than just CO_2 and HCl, it is not suitable as an incinerator catalyst.

The Oxidation of Methylene Chloride over Manganese Dioxide Catalyst

by

Jun Du

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Environment Science

1990

APRROVAL SHEET

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INTRODUCTION

Catalytic oxidation has advantages in the destruction of trace organics to carbon dioxide and water without the addition of supplemental fuel since it can operate below the flammability limit. However, many of these hydrocarbon waste streams contain trace quantities of sulfur, phosphorous and halogen gases which are catalyst poisons. This study addresses the problem by trying to develop catalysts that can oxidize hydrocarbons in the presence of chlorinated compounds at considerable lower temperatures than conventional combustion. As a consequence of reduced operating temperature, the mix of products may be altered.

While a catalyst can facilitate the incineration of halocarbons, in some cases, the halogen in these compounds could damage the active material or the substrate of the catalyst (e.g. Pt on a codierite monolith) (1). Therefore, it is necessary to understand the fundamentals of the catalytic oxidation process for halocarbons not only to optimize halocarbon destruction to less toxic compounds than the feed (activity and selectivity) but also to minimize any catalyst poisoning problem (stability).

The primary objective of this work is to determine if a catalyst system can oxidize low concentrations of chlorinated hydrocarbons at moderate temperatures without being poisoned. In order to determine ultimate effectiveness of a catalytic system, one needs to conduct thermodynamic equilibrium calculations to estimate the distribution of products at "infinite" time. Research to develop an understanding of the primary kinetics and mechanism for catalytic destruction of halogenated compounds with commercial catalysts requires parametric studies of catalytic reaction at operating conditions. To conduct these studies, one needs to assemble necessary analytical equipment, a reaction system, and develop methods to obtain reliable experimental data.

Manufacturers of organic chemicals, petroleum refiners, automotive painting operations, industrial incinerators, etc., generate low concentrations of organic and halogenated compounds in gaseous waste streams. These gaseous waste streams are often diluted with air and emitted to the atmosphere. The proper handling and disposal of these toxic organics can cause health problem directly or through the formation of smog (by the interaction with NO_x and sunlight). These air pollutants are a primary environmental problem facing the world today because of their carcinogenic nature; detrimental impact on the respiratory track and their long term effect on global climate and the ozone layer.

Conventional methods for controlling atmospheric pollutants include incineration, scrubbing and/or adsorption, the products of which are generally disposed of by landfill burial. These methods have drawbacks and are now encountering enormous public opposition. The cost of burial is escalating rapidly due to decreasing availability of suitable sites. High temperature thermal incineration

(1,273 K - 1,773 K) (2), the most widely studied method for the destruction of the chlorinated hydrocarbons, has disadvantages of being capital and energy intensive.

Low temperature catalytic combustion (623 K - 873 K) (2) may be more efficient and selective for the treatment of these organic wastes. Lower costs are anticipated in catalytic incineration because operating temperatures are reduced, allowing more compact equipment made out of less exotic materials of construction.

BACKGROUND

A. Review of the Literature

The thermal incineration and destruction of many chlorinated hydrocarbons are being studied in response to current environmental considerations (3-9).

Some studies have involved noble metals or other oxidation catalysts and supports to treat a number of halogenated hydrocarbon compounds. Bond and Sadeghi (10) studied the destruction of certain chloromethanes and chloroethanes with propane fuel over Pt/Al_2O_3 catalysts. Their result shows that over 90 percent conversion of the CH_2Cl_2, $CHCl_3$, CCl_4, $C_2H_2Cl_2$, C_2HCl_3 and C_2Cl_4 was obtained at temperatures over 450^{o}C. But Bond and Sadeghi do not present data on complete product distributions. In Pope et al., (11) study of the elimination of low concentrations of malodorous air pollutants over Pt-honeycomb catalyst, the reactant 1, 1, 1,- trichloroethane was converted to CO_2 and other chlorinated products at 350 ^{o}C. Only 10 percent of the carbon was converted to CO_2.

Some investigators evaluated transition metals or transition metal oxide catalysts on supports. A chromium impregnated supported catalyst was used in the catalytic oxidation of chlorinated compounds which treated hexachlorobutadiene, hexachlorobezene and hexachloroethane. The chlorine recovery (Cl_2 + HCl/RCl, where R represents all hydrocarbon groups) is 68-100 percent mole fraction and the selectivity of HCl is 0 to 32.7 percent (12, 13). Hydrated nickel oxides and cobalt oxides catalysts were evaluated for the catalytic oxidation of C_2-C_4 halogenated hydrocarbons. Conversions of 45 to 90 percent were obtained for vinyl chloride (VCM), vinylidene chloride (VDCM) and trichloroethane over the nickel oxides (II) and (II, III). At temperatures over 450 ^{o}C, nickel oxide catalysts started to deactivate by thermal sintering. For initial concentration of 46.5 ppm of VCM or VDCM at 107 ^{o}C on the catalyst cobalt oxides (II), 99 percent conversions were measured. Cobalt oxides (II) catalysts deactivated by reacting with the Al_2O_3 support to form inactive $CoAl_2O_4$ when experiencing temperatures over 850 ^{o}C, which is inactive composition (14, 15).

Recently some commercial catalysts were evaluated by Manning (16) in the treatment of chlorinated hydrocarbon compounds. Chromia on alumina catalyst was used in the oxidation of chlorocarbons in an externally pumped recycle fluid bed catalytic reactor. Conversions of 60 to 90 percent was obtained for di, tri, perchloroethlenes at temperatures between 350-550 ^{o}C. Reaction rate expressions were obtained that are first order in the chlorocarbon concentration, between zero and first order in oxygen concentration, and exhibit some inhibition by water.

Pt on honeycomb ceramic structures was used in the oxidation of gaseous pollutants, and volatile chlorinated organic compounds. The catalytic effectiveness (destruction of organic chlorine) was 70 to 90 percent at initial concentrations of 1,000-10,000 ppm (1).

A catalyst's overall effectiveness depends on the spectrum of products (selectivity) from any practical detoxification. The Deacon reaction for the production of Cl_2 by oxidation of HCl has been studied with Cu-based catalyst systems (17-19). The kinetics of oxychlorination of chloromethanes and their destructive oxidation on a supported $CuCl_2$-KCl catalysts shows that the oxychlorination reaction involves the oxidation of HCl. The kinetic patterns of side reactions during deep oxidation of CH_4 and chloromethanes were determined and reactivity of chloromethanes toward Cl_2 was found to be in order (20, 21, 28).

$$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$$

Previous research in the heterogeneous air oxidation of low concentration chlorocarbons has focused on identifying highly active catalysts and reaction products at temperature high enough to essentially achieve complete oxidation. Little work has been reported on the product distribution at intermediate temperatures and the reaction mechanism leading to these products, particularly at temperature below about 400°C. Accordingly, reaction conditions are chosen that result in complete oxidation to H_2O, CO_2 and HCl as predicted by thermodynamic equilibrium calculation. Also, most studies do not report comprehensive analysis of the products of oxidation, which would allow some speculation as to the reaction pathway.

The objective of this study is to investigate the catalytic oxidation of low concentrations of chlorinated hydrocarbons over an available transition metal oxidation catalyst MnO_2. The basic principles and methodology of catalytic oxidation and experimental methods related to the catalyst will be discussed in section C.

B. Chemical Equilibrium Predictions

The equilibrium compositions of the reactant and products, at pressure and temperatures studied experimentally, were calculated to predict the distribution of products and the direction of the oxidizing decomposition process.

Chemical equilibrium is usually determined from thermodynamics by either experimental measurements on equilibrium constants or calculation by the minimization of free energy. The free-energy minimization formulation used in this study is based on the 'Computer Program for Calculation of Complex Chemical Equilibrium Composition, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations'. (22)

For a chemical reaction, we have

$$a\ A + b\ B + c\ C + \ldots \longrightarrow x\ X + y\ Y + z\ Z + \ldots \qquad (2\text{-}1)$$

at chemical equilibrium,

$$\text{del } G = -\ RT \ln K_p \qquad (2\text{-}2)$$

and

$$K_p = \frac{(P_x)^x (P_y)^y (P_z)^z}{(P_a)^a (P_b)^b (P_c)^c} \qquad (2-3)$$

where K is chemical equilibrium constant,

P is partial pressure.

The chemical equilibrium calculation were conducted to determine potential product distributions at the appropriate experimental conditions of this study. Two types of calculations were carried out. The first type used temperature and pressure to get product distribution for comparison with those obtained experimentally. The second type calculated possible temperature rise by estimating the adiabatic temperature of the system. The results were fed back to adjust direction of operation conditions and help to estimate final distributions of product constituents.

C. Basic Principles of Catalysis

1. General Description of a Catalyst

Many commercial heterogeneous catalysts are composed of active catalytic components supported on refractory oxides or carbons. An unsupported-catalyst is a metal or metal oxide powder. Molecules vary in size and chemical structure, so different catalysts are necessary for different reaction processes. The optimization of a catalyst is specific for each reaction and operating condition.

Therefore, determination of performance of a catalyst is dependent on practical reaction processes.

2. Catalytic Processes and Kinetics Characterization

In a catalytic process, reactants must interact with the "active site" on the catalyst, the term "active site" is thought to be that site (or sites) on the catalyst surface in which chemisorption and reaction occur. Basically, a catalytic process includes:

1. Bulk diffusion: reactants must pass through stagnant film from the gas or liquid phase.

2. Pore diffusion: a reactant diffuses or transports through pore structure to active sites.

3. Chemisorption: a reactant chemically adsorbs on to active site i.e., by bonding.

4. Chemical reaction: a reactant converts to a product(s) on the active site.

5. Desorption: a product(s) desorbs from the active site.

6. Product pore diffusion: a product diffuses from pore sites.

7. Product diffusion: a product diffuses through the film to the gas or liquid phase.

Steps 1 and 7 are controlled by mass transfer; steps 2 and 6 are controlled by pore diffusion; steps 3, 4 and 5 are controlled by chemical reaction (23). The physical and chemical properties of catalysts and operating conditions that control the rate of reaction should be carefully chosen. Much research is required to optimize the properties of a catalyst and the conditions for its use. The generally applicable test for rate limiting phenomena is an Arrhenius plot from which activation energies are determined.

A general plot depicting the various rate parameters as a function of temperature is shown in Figure 1. Figure 2 illustrates a conversion versus temperature profile (1). The relationship used in plotting Figure 1 is the Arrhenius expression:

$$k = A \exp(-E/RT) \tag{2-4}$$

$$\ln k = \ln A - (E/R)(1/T) \tag{2-5}$$

where,

k = rate constant,

A = pre-exponential constant,

E = activation energy,

R = gas constant,

T = absolute temperature.

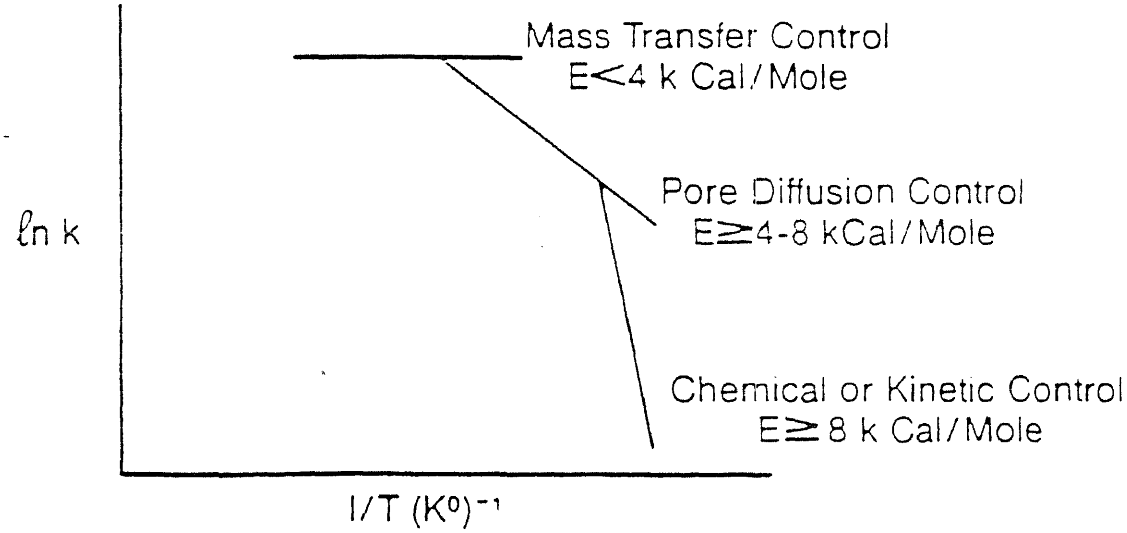


Figure 1 Arrhenius Equation

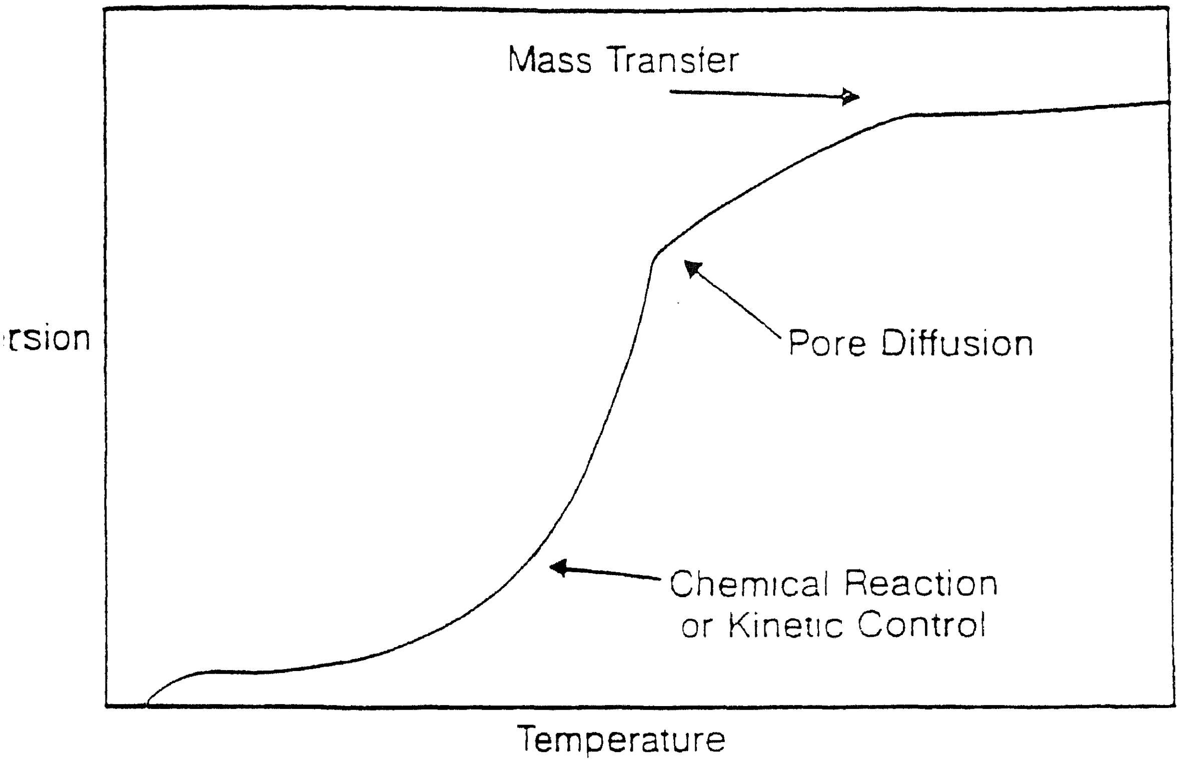


Figure 2 Conversion of reactant as a function of temperature showing rate controlling regimes

The calculation of the activation energy, E, from the slope of the Arrhenius plot allows an assessment of the rate limiting step. From Figure 2 it is evident that reactions controlled by chemical kinetics are most sensitive to temperature, while mass transfer controlled reaction are the least. Another empirical identification of the diffusion zone (mass transfer) is:

$$k \propto T^{n} \tag{2-6}$$

where, k is rate constant, n is 1.7, and T is temperature in degrees K. It should be noted that the theoretical temperature dependence of diffusion, based on the kinetic theory of gases is 1.5 (24).

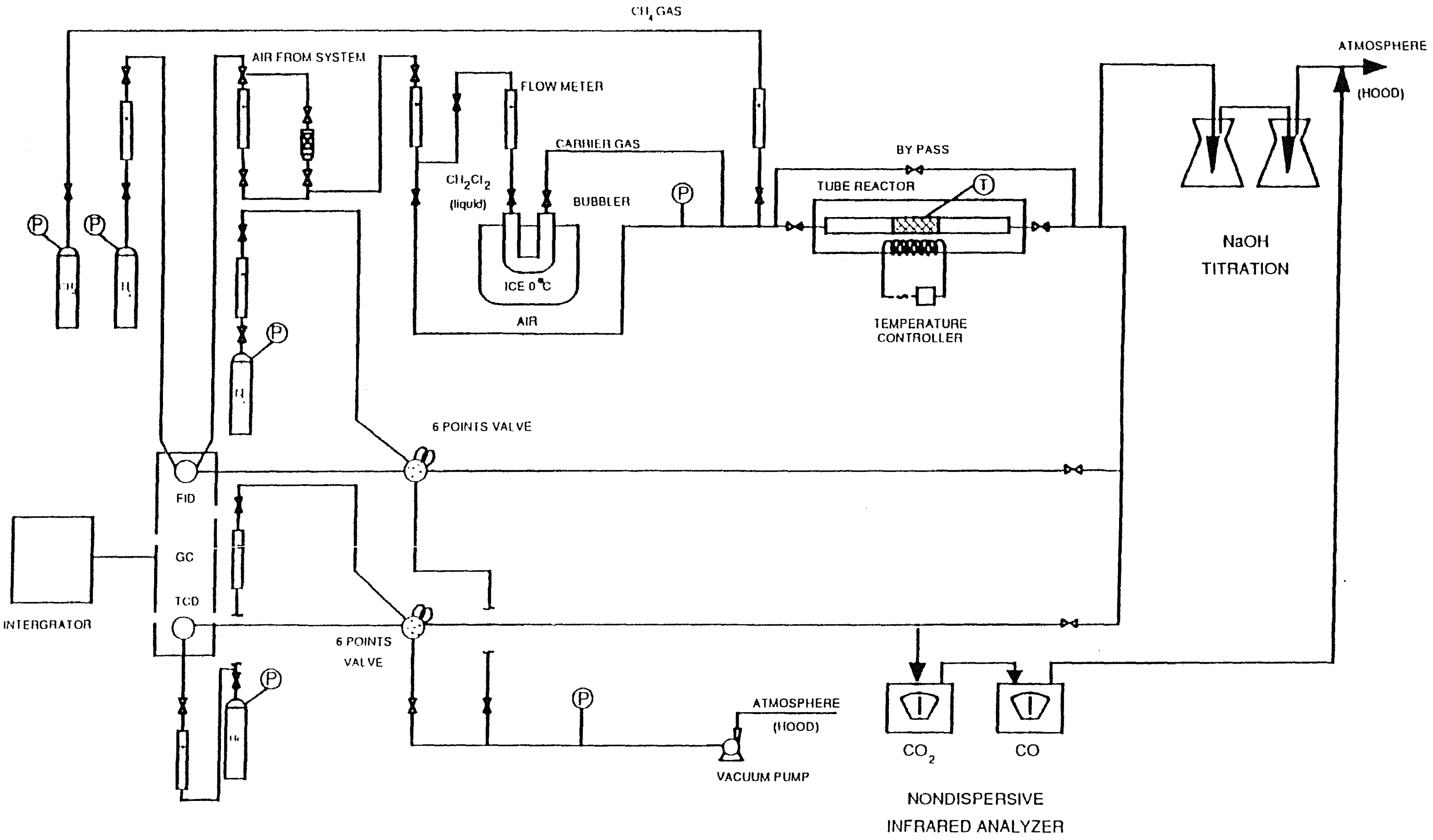
EXPERIMENTAL APPROACH

A. Experimental Apparatus

The experimental apparatus flow schematic is shown in Figure 3. A tubular flow reactor system was set up to study the reaction mechanism. The reactor consists of a quartz tube (7 cm I.D. and 0.5 meter in length) residing in a tubular furnace containing known amounts of high surface area MnO_2 (0.2, 0.4, 0.6, 0.8 g, and 0.105 g diluted with silica gel up to the same volume as the 0.4 g sample).

A cooled glass bubbler containing the chlorinated hydrocarbon reactant (dichloromethane) in liquid form was connected between the air feed line and the reactor. The reactant was carried into the reactor by "dry grade" air, which was dried by active carbon, or chemical analytical grade N_2. The dry gas picks up a fixed concentration of reactant (CH_2Cl_2) via a saturation bubbler maintained at 0^oC by using an ice-water bath. The reactant was then swept into the reactor through a heated inlet line. In order to achieve a lower concentration of CH_2Cl_2, an additional amount of air or N_2 was mixed into the reactant gas mixture at a junction after the bubbler. The laboratory reactor furnace (Hoskins electric furnace made by Hoskins MFG. Co. Type FA-120) provided an isothermal profile over the middle 3 cm region of the quartz tube. In order to operate at a reasonable reaction rate, catalysts were brought up to light-off temperatures, usually about 513 K. The furnace temperature was controlled with a voltage controller GC module made by Burling Instrument Co. Summit, NJ. Catalyst

FLOW SCHEMATIC OF CATALYTIC OXIDATION UNIT

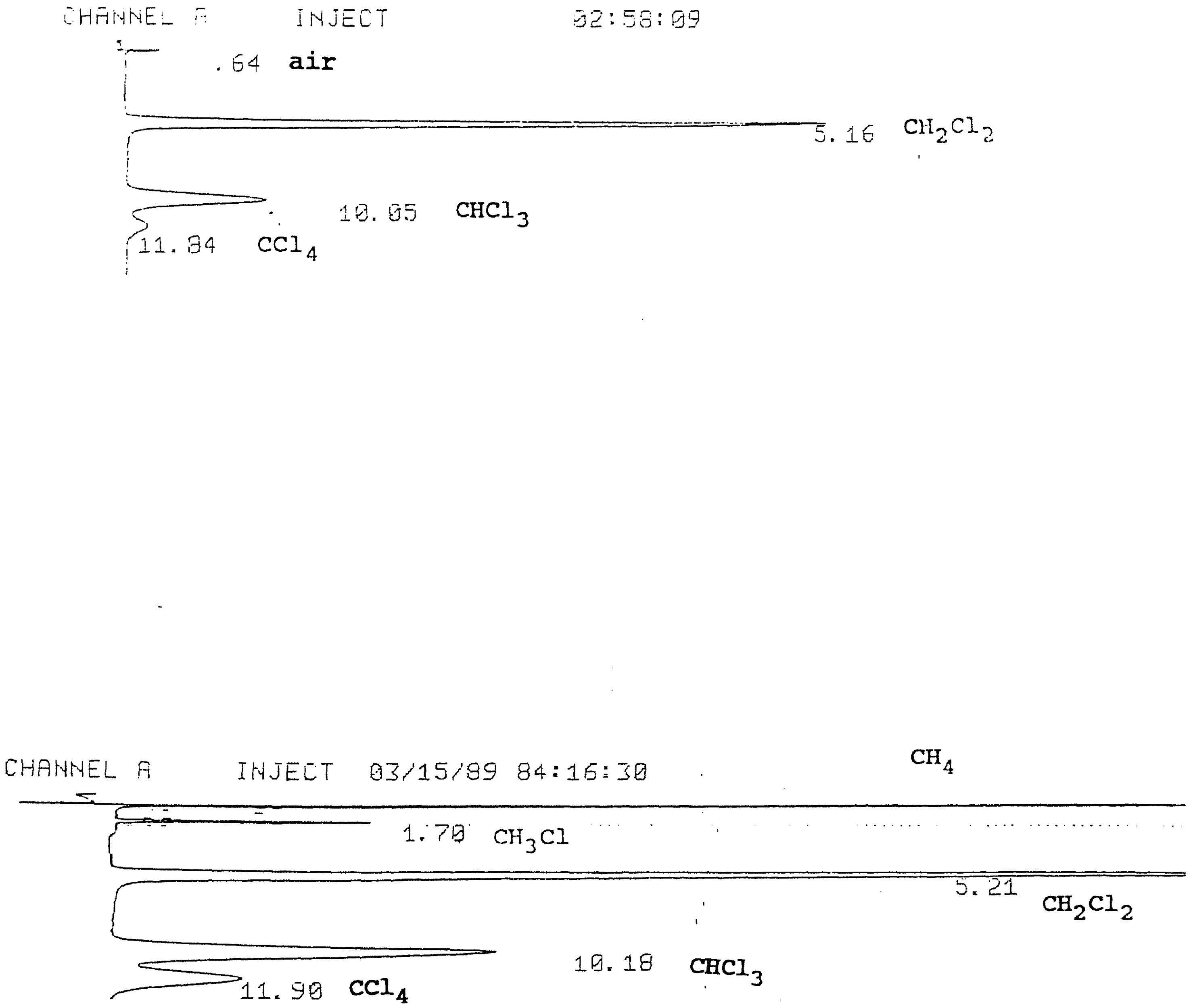


temperature was measured with an chromel-alumel (K-type) thermocouple touching the downstream portion of the bed. Gas flow rates were adjusted by needle valves. A manometer was used for the measurement of catalyst packed bed pressure drop. Part of the exhaust gas was directed to the analytic train using a vacuum pump, The rest was discharged to a laboratory hood (no train back to GC from the exhaust duct).

B. Analytical Techniques

Part of the effluent product stream was pulled by a vacuum pump into a 1.382 ml sample loop of a six port gas sampling valve. The carrier gas (N_2) then picked up the sample and injected it into an on-line gas chromatograph (Perkin-Elmer model 910) with FID detector. A 6', 1/8" column packed with 3% SP1500 on 80/100 mesh Carbopak-B was used to analyze the reactant and products CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The integrator (Spectra-Physics model SP4290) was used as both a recorder and integrator. Figure 4 presents typical peak resolution and retention time for the reactant and products. GC/mass was used for qualitative identification and verification of product distribution by batch collection of the product stream in a sampling cylinder. The Beckman continuous nondispersive infrared analyzers (model 864 and model 865) were used to measure trace quanatities of carbon monoxide and carbon dioxide. Hydrogen chloride was collected in two impingers, each containing measured amounts of a standard solution of sodium hydroxide and a little phenolphthaleim as an end-point indicator. When the first impinger indicated that the

Figure 4 Typical GC Resolution and Retention Time for CH_2Cl_2, $CHCl_3$, and CCl_4 Sample Peaks



end-point had been obtained, the concentration of HCl was analyzed by titration of the second impinger using the standard solution of HCl and calculation of the HCl concentration in the first impinger. In this way, one prevents HCl from escaping through NaOH solvent because of high flow rate. Water production was estimated by difference in the hydrogen material balance.

C. Catalyst Materials:

The order of activity of simple metals or metal oxides for the complete oxidation of chlorinated hydrocarbon compounds was summarized by Ramanathan et al. (27), :

$$Co \sim Cr > Mn > Cu > Ni > Pt > V > Mo$$

This ranking approximates the more general one of Germain (25). MnO_2 is 2nd in activity in the list, and is available as a high surface area (112 m^2/g) commercial product. Therefore, MnO_2 power (25-1370 tech. gr. less than 325 mesh, Strem Chemicals, Inc., Newburyport, MA 01950) was chosen for testing in this application. Its properties are summarized in Table 1.

TABLE 1 CATALYST PROPERTIES

Property	Value	Note
BET Surface Area	112 m^2/g	
Apparent Diameter	7.1 ± 0.2 um	(Microscope)
Bulk Density	1.06 g/cm^3	
Theoretical Density	5.03 g/cm^3	
Melting Point	808 K	(Decomposes)

D. Experimental Procedures

1. Analysis Conditions and Materials

GC : Perkin Elmer Model 910

Oven Temperature: 185 °C (isothermal)

Attenuation of Amplifier: 8

Range of Amplifier: 10

FID detector:

Temperature: 200 °C

Gas flow rate: (Calibrated by a soap film bubble meter)

Hydrogen: 30 cc/min at 30 psia

Nitrogen: 30 cc/min at 30 psia

Dry Air: 300 cc/min at 30 psia

Nondispersive infrared analyzers:

Range: 1

CO gain: 5

CO_2 gain: 20

Dry air flow rate: 100 cc/min at 1 atm

Titration:

NaOH solution: two 20 ml/impinger 0.01 M

HCl solution: 50 ml/each time 0.01 M

2. Experimental Procedures

1. Studies were conducted with 0.01 mole percent dichloromethane in 99.99 mole percent air as a function of temperature (450-800 K) and space velocities 6.67, 3.33, 2.22, 1.67 v/v/sec (Flow rate/Active Catalyst Volume). Product distributions were obtained for each experiment.

2. The effect of 2.33 mole percent methane on the oxidation reaction of 0.01 mole percent dichloromethane,

with 97.66 mole percent air was also studied over the same weight of catalyst (0.4 g) and at the same operation conditions as the CH_2Cl_2/air only. Product distributions were measured for this system.

3. The effect of space velocity was studied to obtain chemical kinetic parameters at different catalyst operating regions such as kinetic and mass transfer limitation.

4. Catalytic oxidation of methane and air at the same conditions as above.

5. The Contribution of an empty reactor (without active material) to conversion was determined by studying the reaction of the same feed composition over the temperature range outlined above.

6. The conversion of CH_2Cl_2 on a mixture of 0.105 g MnO_2 diluted with silica gel was studied. The volume of solid material was kept constant for the 0.4 g pure MnO_2 and the 0.105 g MnO_2/silica gel catalysts.

7. The effect of oxygen was determined by running in CH_2Cl_2/pure N_2 at the same condition of temperature and space velocity 3.33 v/v/sec.

8. Catalyst activity maintenance was checked by running an experiment with a new charge of catalyst at the same condition of one of experiments with the previous catalyst charge. In no case did we observe excessive aging which would invalidate any of the results. In experiments where the catalyst temperature exceeded 700 K and sintering may have occured, the charge was replaced.

E. Error Analysis

Accuracy of GC and infrared analyzer calibration relative response factor were estimated to be less than 5 percent. Temperature measurement error was ± 0.1 ^{o}C; pressure measurement error was ± 0.5 psia. Titration error was estimated to be about 0.5 percent which results from volumetric tube reading and preparation of the standard solutions. Therefore, GC and infrared analyzer errors are the primary sources of error in these experiments.

The relative replication errors (precision) of chlorinated compounds measured by GC are shown in the following three tables:

TABLE 2 REPLICATION OF DICHLOROMETHANE

Sample No/T	Rep. No	Results of CH_2Cl_2 ppm	Mean ppm	Sum of Sq. deviation	Note
1 501K	2	94.6, 95.4	95	0.32	0.3 sec CH_2Cl_2 + CH_4 + air
2 525K	3	74.7, 73.0, 74.0	73.9	1.46	
3 721K	3	41.6, 40.9, 38.6	40.4	4.92	
4 588K	3	60.8, 58.6, 58.3	59.2	3.66	0.15 sec CH_2Cl_2 + air
5 650K	2	63.8, 68.0	65.9	8.82	
6 660K	3	28.6, 28.9, 28.3	28.6	0.18	0.6 sec CH_2Cl_2 + air
7 705K	2	34.5, 36.9	35.7	2.88	CH_2Cl_2 + air
8 670K	2	25.9, 25.5	25.7	0.08	
9 595K	2	45.8, 45.4	45.6	0.08	
Sum	22			22.4	

$$C.L. \text{ for } \mu = \bar{x} \pm \frac{z\sigma}{\sqrt{n}} \qquad (2\text{-}6)$$

n = the average of n replication measurements,

$\bar{x}$ = mean value,

C.L. = confidence limit.

$$S = \sqrt{\frac{22.4}{22 - 9}} = 1.3 \text{ ppm}, \quad (26)$$

if took 95 % C.L., z = 1.96, n = 2, in this case, the standard deviation could be replaced by s (26);

$$\text{for 1,} \quad 95 \pm \{\frac{1.96 * 1.3}{1.414}\} = 95 \pm 1.8 \text{ ppm;}$$

for 3, n = 3, 40.4 ± 1.5 ppm.

TABLE 3 REPLICATION OF CHLOROFORM

No of Rep.	Results CH_2Cl_2 ppm	Mean ppm	Sum of Square Deviation	Note
2	1.22, 2.05	1.64	0.35	Same as Table 2
3	10.6, 10.9, 10.7	10.7	0.05	
3	30.2, 30.4, 30.5	30.4	0.05	
3	18.1, 19.5, 20.2	19.2	2.30	Same as Table 2
2	19.2, 19.4	19.3	0.02	
3	28.7, 29.2, 29.0	29.0	0.13	Same as Table 4
2	32.7, 31.7	32.2	0.50	Same as Table 2
2	32.1, 31.2	31.7	0.41	
2	22.8, 25.0	23.9	2.60	
22			6.41	

the same as Table 2, S = 0.70 ppm.

For 5, 19.3 ± 0.97 ppm at 95 % C.L.

TABLE 4 REPLICATION OF CARBON TETRACHLORIDE

No of Rep.	Results of CH_2Cl_2 ppm	Mean ppm	Sum of Square Deviation	Note
3	4.4, 4.2, 4.4	4.33	0.03	Same as
3	5.9, 6.2, 6.5	6.2	0.18	Table 4
3	6.1, 6.2, 6.4	6.23	0.05	Same as
2	3.0, 2.7	2.85	0.05	Table 4
2	17.2, 17.4	17.3	0.02	Same as Table 4
2	9.2, 9.2	9.2	0.0	Same as
2	12.9, 12.9	12.9	0.0	Table 4
2	8.5, 8.7	8.6	0.02	
19			0.35	

(Standards: Scotty IV, contents 3.7 L, 240 psig at 70 F^o, Sccott Specialty Gases, Plumsteadvill, PA 18949. CO, CO_2: Can mix 48 in N_2; CH_2Cl_2, $CHCl_3$, and CCl_4: blend 1, No 46665-4EL in N_2.)

$$S = \sqrt{\frac{0.35}{19 - 8}} = 0.17 \text{ ppm}$$

the same as Table 2, for 9,

8.6 ± 0.25 ppm at 95 % C.L.

Therefore, the relative replication error is about 4 %. Material balance of Cl: 100 ± 5 % Material balance of C : 95 ± 6 % (see Tables 7 and 8) were considered acceptable.

RESULTS

A. Results of Chemical Equilibrium Calculations

1. Temperature Effect on Chemical Equilibrium

The actual experimental compositions of 0.01 mole percent dichlomethane (CH_2Cl_2) and 99.99 mole percent air (O_2 + 3.78 N_2), were employed in the calculation. The effect of varying temperature over the range from 400-800 K at atmospheric pressure was studied. Table 5 shows that the major products of the equilibrium mixture, except for excess oxygen and nitrogen, were carbon dioxide, water, hydrogen chloride (HCl) and chlorine gas (Cl_2) as well as a very much lower concentration of nitrogen dioxide (NO_2). Chloromethane, dichloromethane, chloroform, carbon tetrachloride, and some other NO_x compounds were less than 1.0*E(-15) mole fraction. Chlorinated hydrocarbons are predicted to be at lower concentration at equilibrium then was found experimentally. The distribution of major products carbon dioxide, water, hydrogen chloride, chlorine gas and nitrogen dioxide versus temperature are depicted in Figure 5.

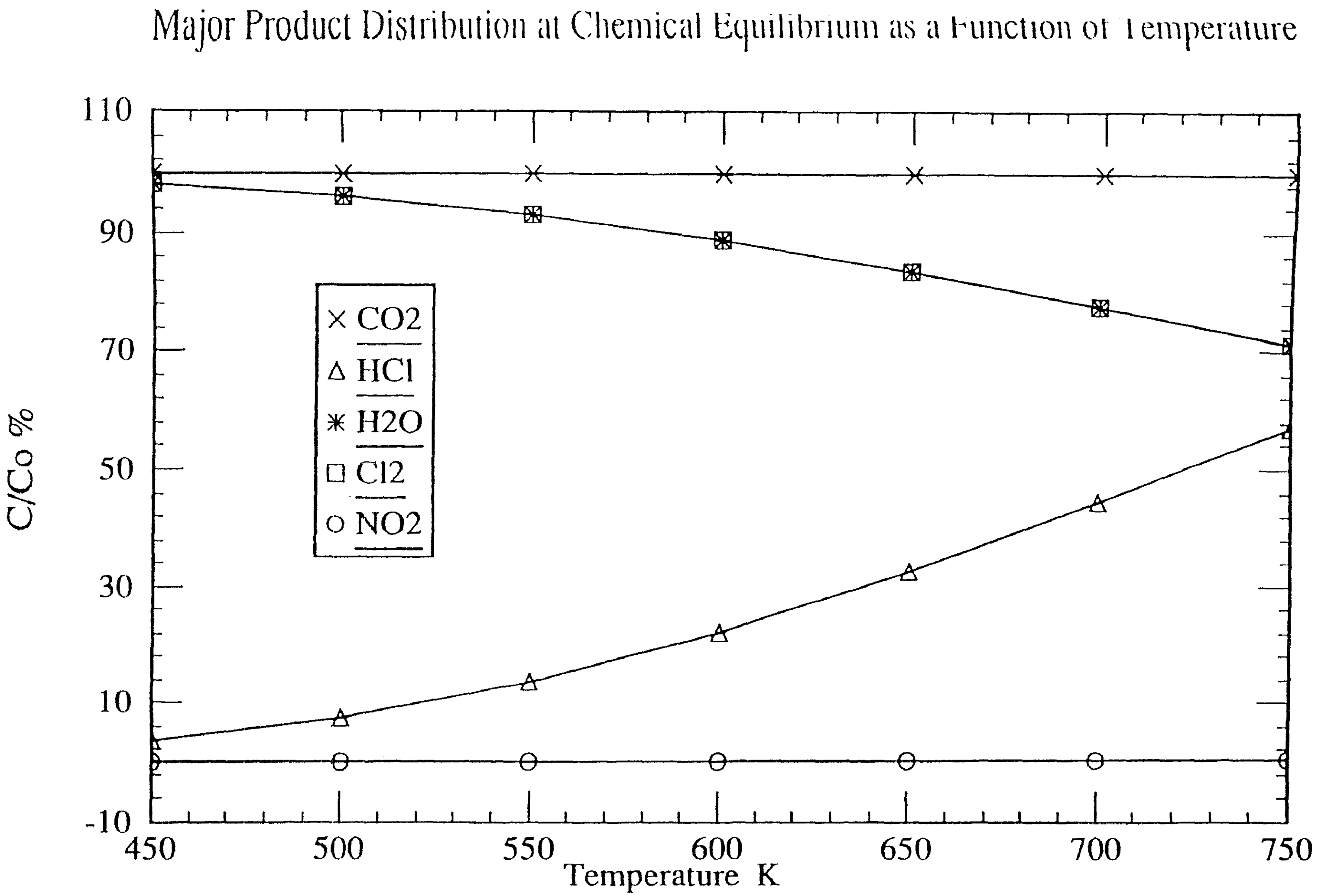
As temperature increased, HCl increased, CO_2 remained almost constant, and Cl_2 and H_2O decreased slightly. Hydrogen chloride is slightly affected by temperature, while carbon dioxide and water are essentially unaffected by temperature. In addition, the low level of nitrogen dioxide indicates that catalytic oxidation can minimize NO_x production because of low temperature operation and absence of nitrogen compounds in the feed.

TABLE 5 MAJOR EQUILIBRIUM PRODUCTS FOR CH_2Cl_2 OXIDATION WITH AIR (EXCEPT N_2 AND O_2)

Unit: ppm

Temp. K	450	500	550	600	650	700	750
CO_2	99.8	99.8	99.8	99.8	99.8	99.8	99.8
HCl	3.51	7.45	13.6	22.1	32.6	44.5	57.1
Cl_2	98.1	96.1	93.0	88.8	83.5	77.6	71.3
H_2O	98.1	96.1	93.0	88.8	83.5	77.6	71.3
NO_2	0.01	0.03	0.06	0.11	0.18	0.28	0.41

Note: The condition of CH_2Cl_2 (0.01 mole percent) and air (99.99 mole percent) at atmospheric pressure.



Co is the initial concentration of CH2Cl2 at CH2Cl2 and air system

Figure 5. Major product distribution at chemical equilibirum as a function of temperature

2. Methane Effect on Chemical Equilibrium

Table 6 shows that the concentration of products CO_2 and H_2O increased very considerably when CH_4 was included in the calculation, which were 0.01 mole percent CH_2Cl_2, 2.33 mole percent CH_4 and 97.66 mole percent air at the same T, P conditions as Table 5. The adiabatic temperature increased from 454 to 1095 K, which indicates CH_4 is a hydrocarbon fuel that converts to CO_2 and H_2O and releases heat energy at chemical equilibrium. But, under isothermal conditions, major products CO_2 and H_2O still were unaffected by temperature as summarized in Figure 6. The product trend was similar to that in the absence of CH_4, as temperature increased, HCl increased, whereas Cl_2 decreased, NO_2 remained at a trace level. Figure 7 summarizes this trend.

B. Experimental Results

1. Temperature Effect on the Reaction

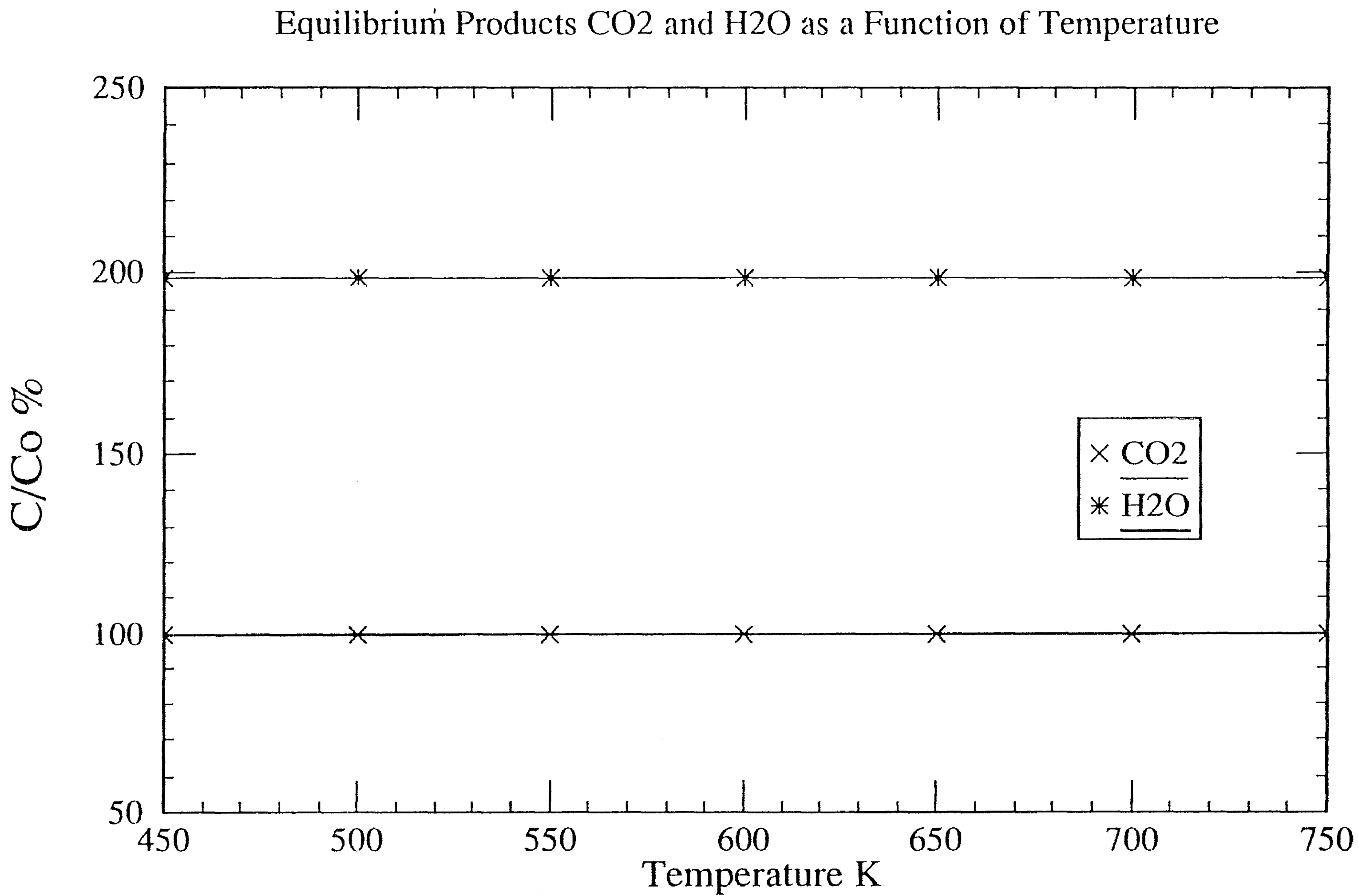
In the oxidation of dichloromethane at space velocity 3.33 v/v/sec and the CH_2Cl_2/air system, it was found that in the temperature range of 450-513 K, catalytic reaction was observed but at a very low rate. The major products were carbon dioxide, hydrogen chloride and water with trace amounts of chloroform. As temperature was increased over 513 K, conversion increased rapidly. Apparently, catalytic light-off (start of activity) temperature at 513 K was achieved. At higher temperatures, water and chloroform increased substantially, and carbon tetrachloride was found. At temperatures between 625-700 K, conversion of dichloromethane became gradually independent of temperature.

TABLE 6 MAJOR EQUILIBRIUM PRODUCTS FOR CH_2Cl_2 OXIDATION WITH AIR IN THE PRESENCE OF CH_4 (EXCEPT N_2 AND O_2)

Unit: ppm

Temp. K	450	500	550	600	650	700	750
CO_2	23300	23300	23300	23300	23300	23300	23300
HCl	67.9	117	158	181	191	196	198
Cl_2	66.1	41.7	21.3	9.71	4.43	2.15	1.12
H_2O	46500	46500	46500	46500	46500	46500	46500
NO_2	0.01	0.02	0.04	0.08	0.13	0.20	0.29

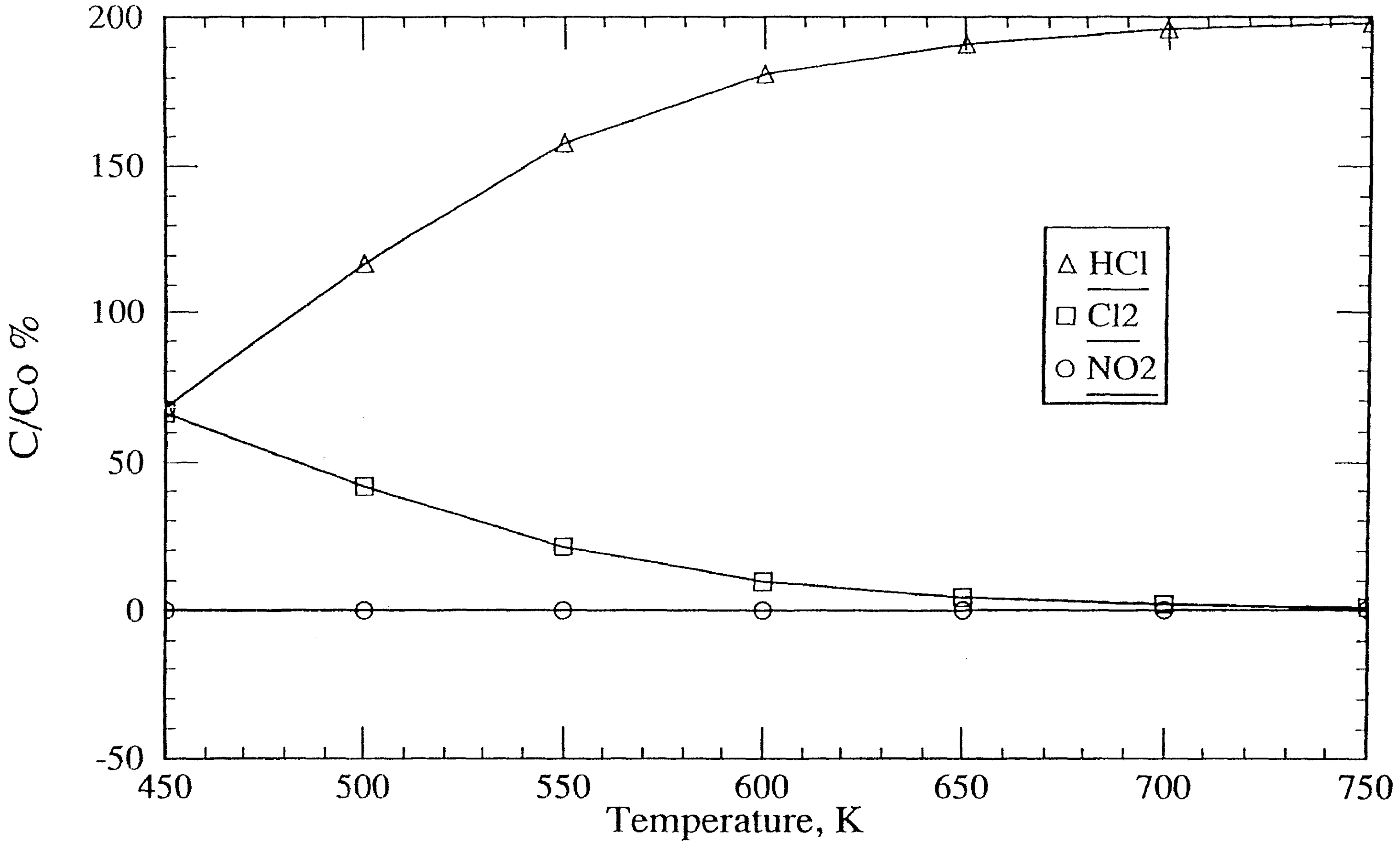
Note: Under the condition of CH_2Cl_2 (0.01 mole percent) and CH_4 (2.33 mole percent) and air (97.66 mole percent) at atmospheric pressure.



Co is initial concentration of CH2Cl2 and CH4 at CH2Cl2, CH4 and air system.

Figure 6. Equilibrium products CO_2 and H_2O distribution as a function of temperature

Equilibrium Products Cl2, HCl, and NO2 Distribution as a Function of Temperature



Co is the initial concentration of CH2Cl2 at CH2Cl2, CH4 and air system

Figure 7. Equilibrium products Cl_2,HCl and NO_2 distribution as a function of temperature

Over 700 K, the retention (defined as 1 - conversion) of dichloromethane became almost constant with temperature. The products chloroform, carbon tetrachloride as well as water also remained fairly constant, but hydrogen chloride increased slightly. The retention of dichloromethane as a function of temperature in the CH_2Cl_2 + air system, at the space velocity 3.33 v/v/sec, is shown in Figure 8. The variation of concentrations of carbon dioxide and water with temperature are shown in Figure 9. The variation with temperature of chlorine containing compounds: chloroform, carbon tetrachloride and hydrogen chloride are shown in Figure 10.

The experimental data and the material balances for chlorine and carbon for the CH_2Cl_2 and air system, at the space velocity 3.33 v/v/sec (residence time 0.3 sec), and linear velocity 1.83 cm/sec is shown in Table 7. At higher temperatures, carbon balances decreased to 80 percent. This discrepancy was due to carbon monoxide production, which could not be detected in the analytical system.

The retention of dichloromethane versus temperature at space velocities 6.67, 2.22, 1.67 v/v/sec (residence times of 0.15, 0.45 and 0.6 sec) are shown in Figures 11, 12, and 13. The conversion of dichloromethane increased at lower space velocities (higher residence times) with increasing temperature. The retention of dichloromethane at a space velocity 2.22 v/v/sec (residence time 0.45 sec) became less

TABLE 7 OXIDATION OF DICHLOROMETHANE WITH AIR AT A SPACE VELOCITY OF 3.33 v/v/sec AND 0.4 g OF MnO_2 CATALYST

Temp. K	Concentration of C/Co %						Mass Balance	
	CO_2	CH_2Cl_2	$CHCl_3$	CCl_4	H_2O	HCl	Cl	C
450	0.0	0.0	0.0	0.0	0.0	0.0		
473	1.8	94.7	0.8		3.6	2.2	97	97
558	4.8	70.3	11.7	3.3	23.1	2.0	93	88
567	4.9	68.2	14.6	4.1	23.4	3.4	100	90
617	6.1	68.0	15.6	4.6	23.7	1.0	101	94
637	6.6	59.2	18.2	6.2	28.9	2.4	99	90
654	7.3	56.6	19.7	7.0	31.5	0.5	100	91
663	7.9	44.2	23.8	7.3	39.4	4.4	97	83
669	7.5	43.8	25.7	9.7	39.4	2.9	103	87
672	7.8	45.2	22.3	7.3	43.6	3.7	95	83
677	7.8	41.6	26.2	9.2	43.9	1.6	100	85
700	8.2	36.9	31.1	9.2	45.5	3.7	104	85
708	8.4	34.5	32.7	9.2	48.1	3.7	104	85
721	8.4	25.4	35.9	11.3	53.4	3.5	104	81
729	9.5	19.2	36.4	13.8	61.8	2.5	103	80
737	10.0	18.8	37.5	13.5	61.0	4.0	104	80
744	10.5	19.0	37.2	13.3	61.5	2.9	103	80

Note: Co is initial concentration of CH_2Cl_2, at atmospheric pressure.

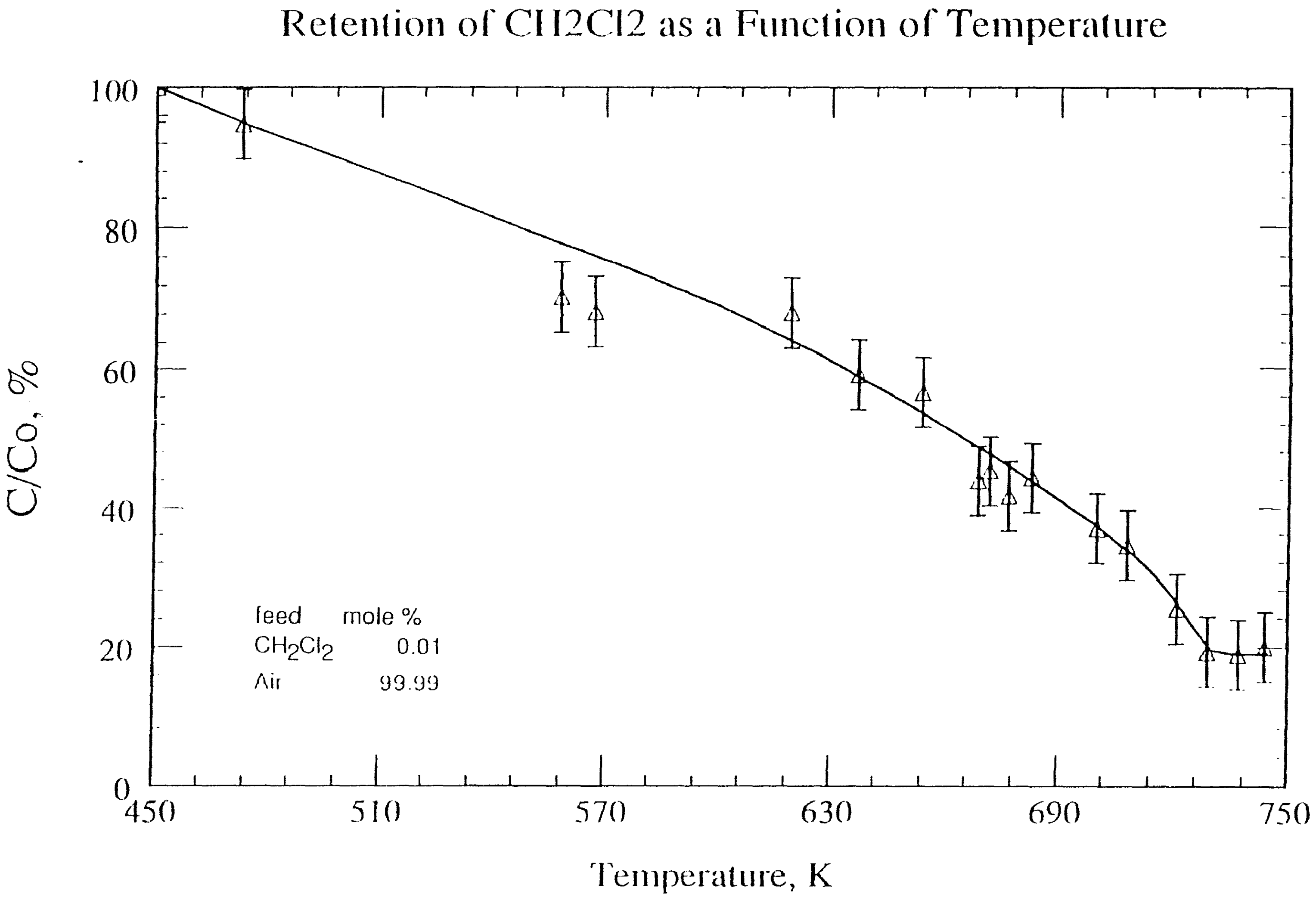
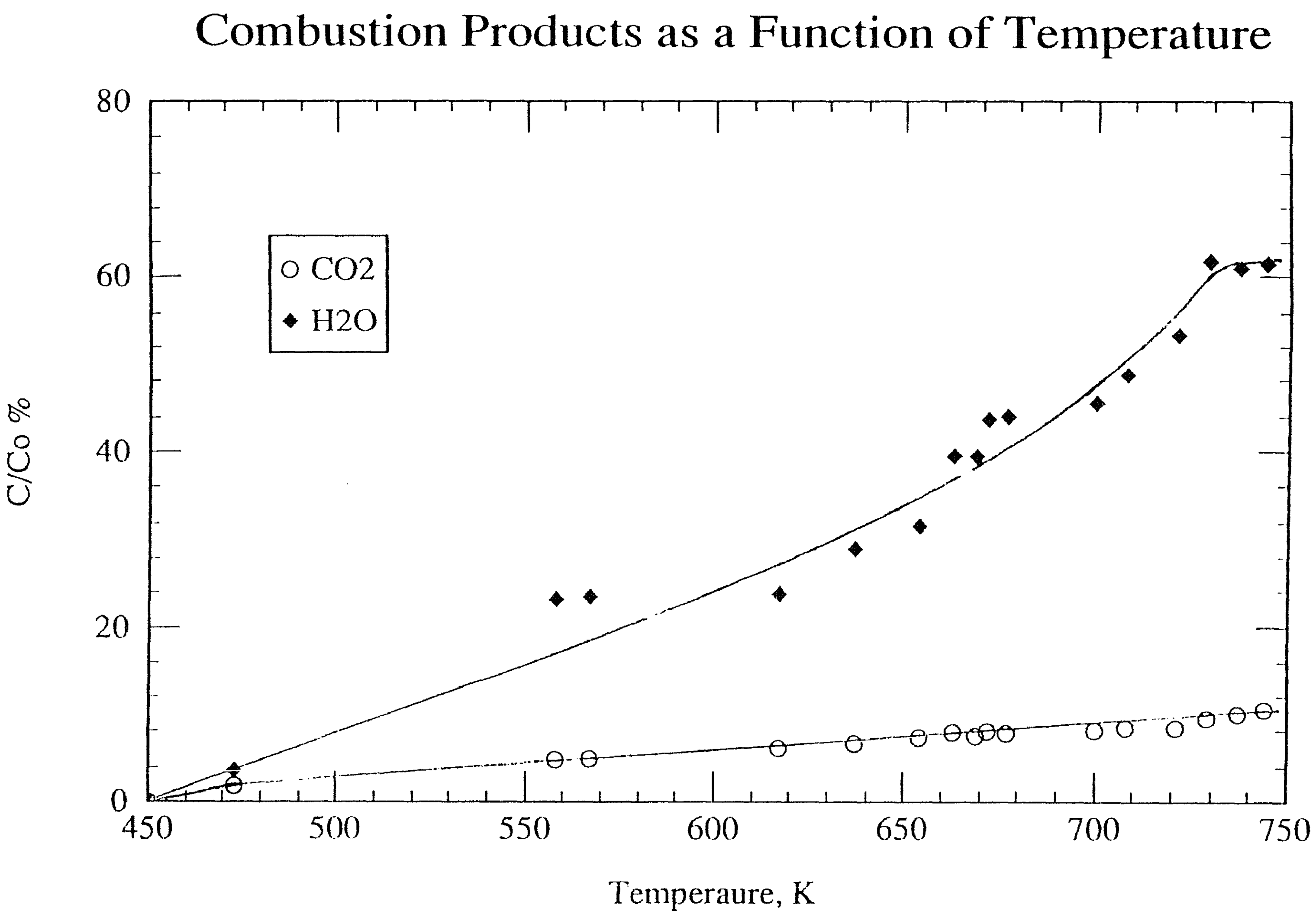
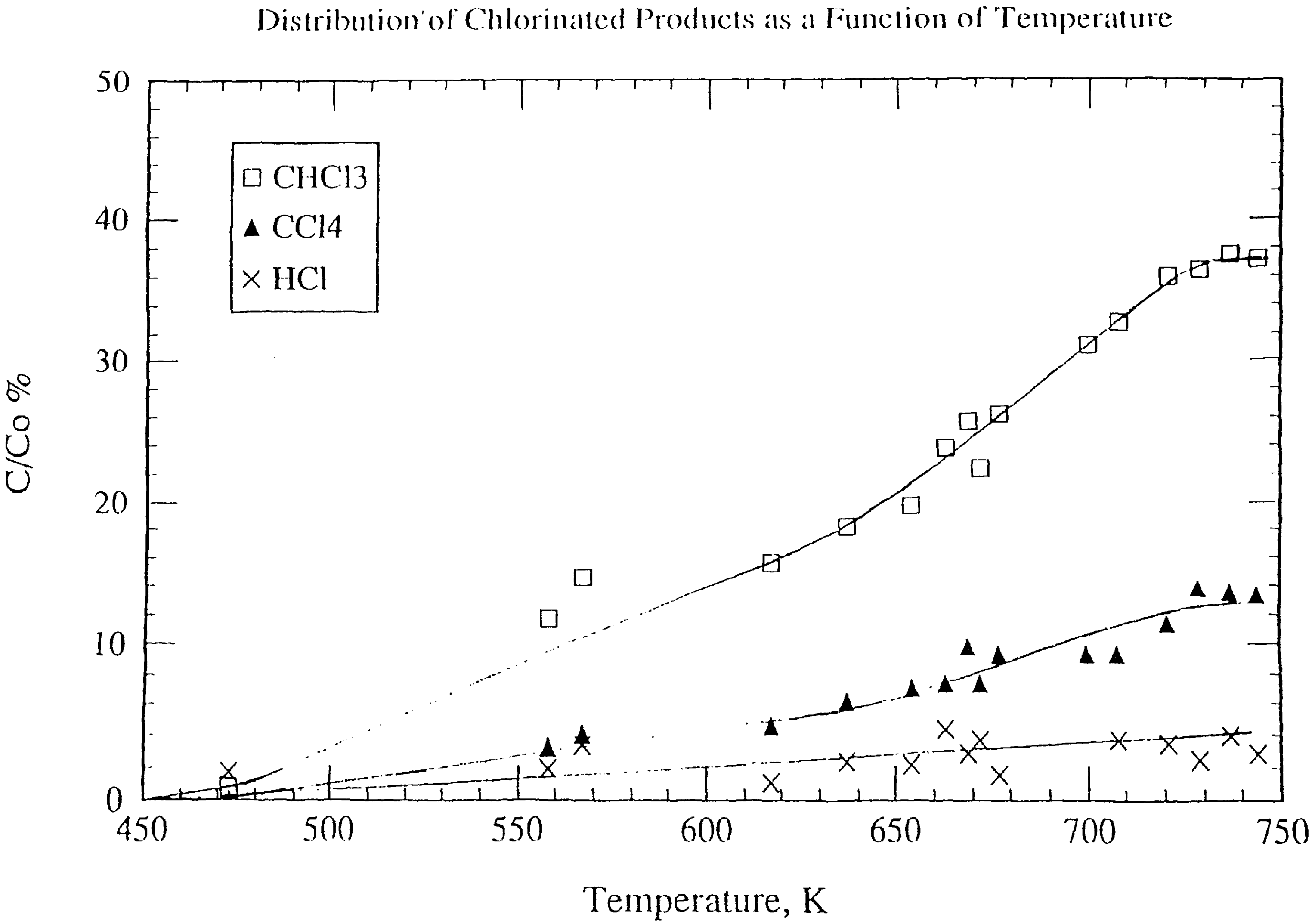


Figure 8. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 3.33 v/v/sec



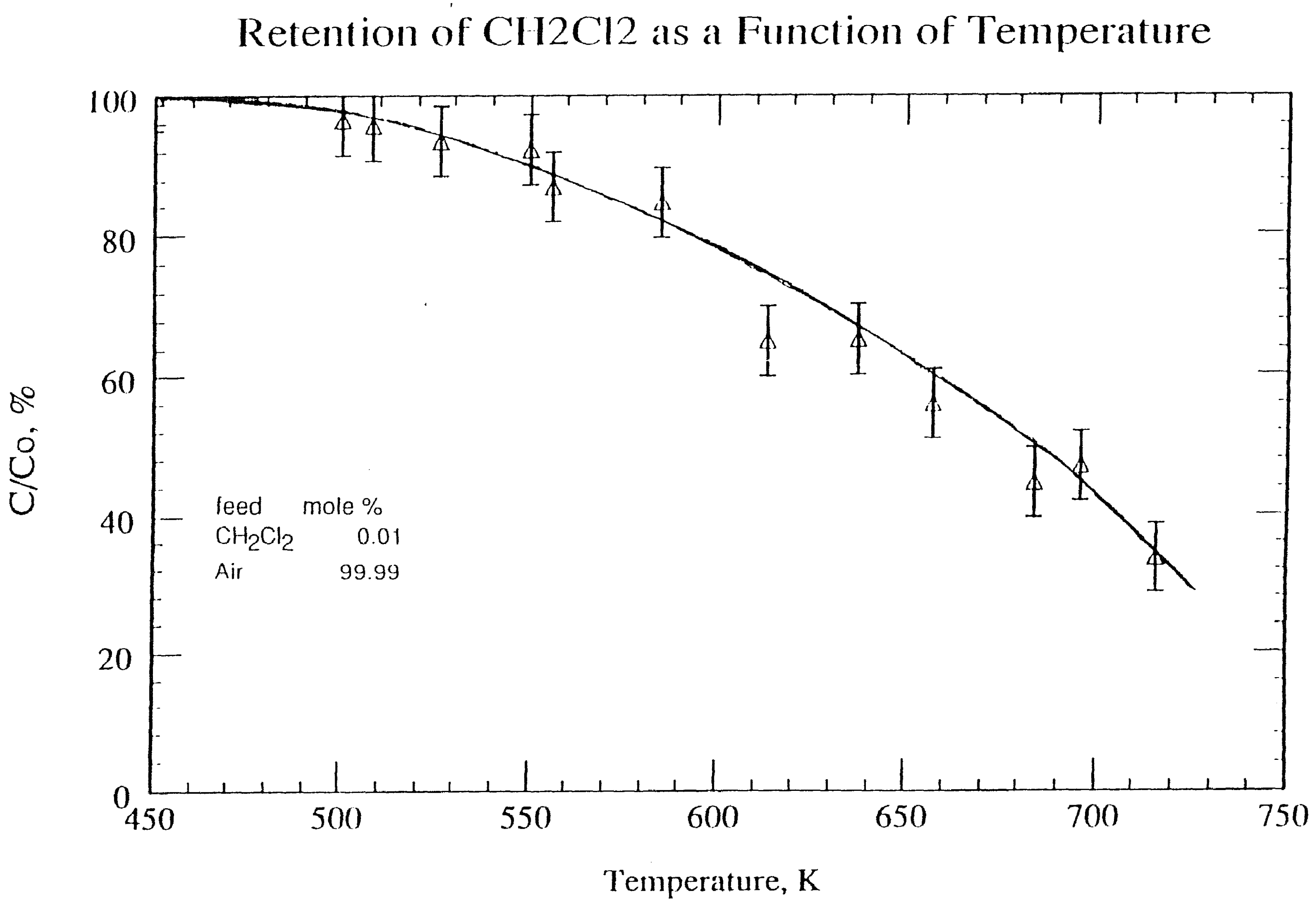
Co is the initial concentration at CH2Cl2+air

Figure 9. Combustion products as a function of temperature at a space velocity of 3.33 v/v/sec



Co is the initial concentration of CH2Cl2 at CH2Cl2 + air

Figure 10. Distribution of chlorinated products as a function of temperature at a space velocity of 3.33 v/v/sec



Retention of CH2Cl2 as a Function of Temperature

Figure 11. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 6.67 v/v/sec

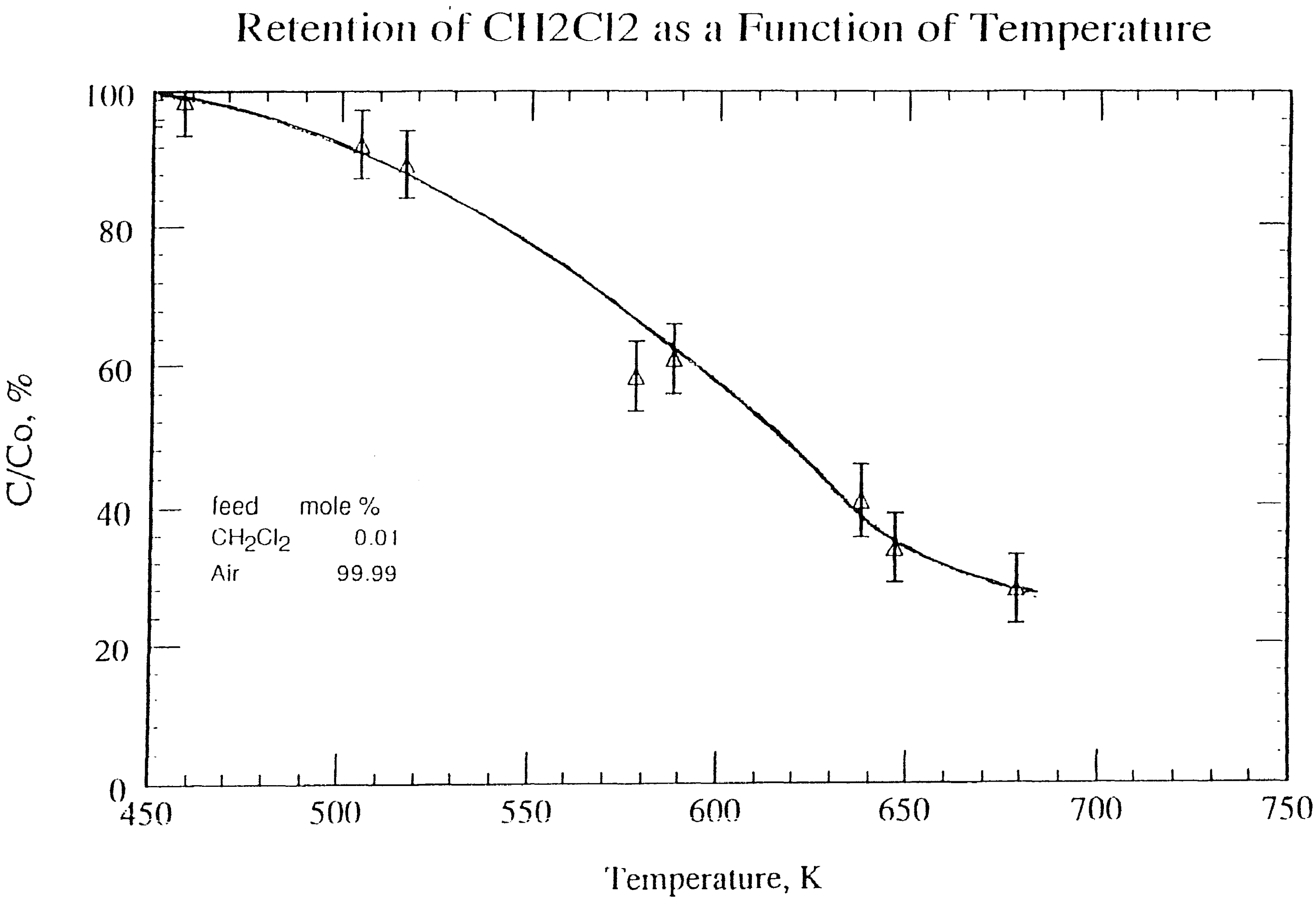


Figure 12. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 2.22 v/v/sec

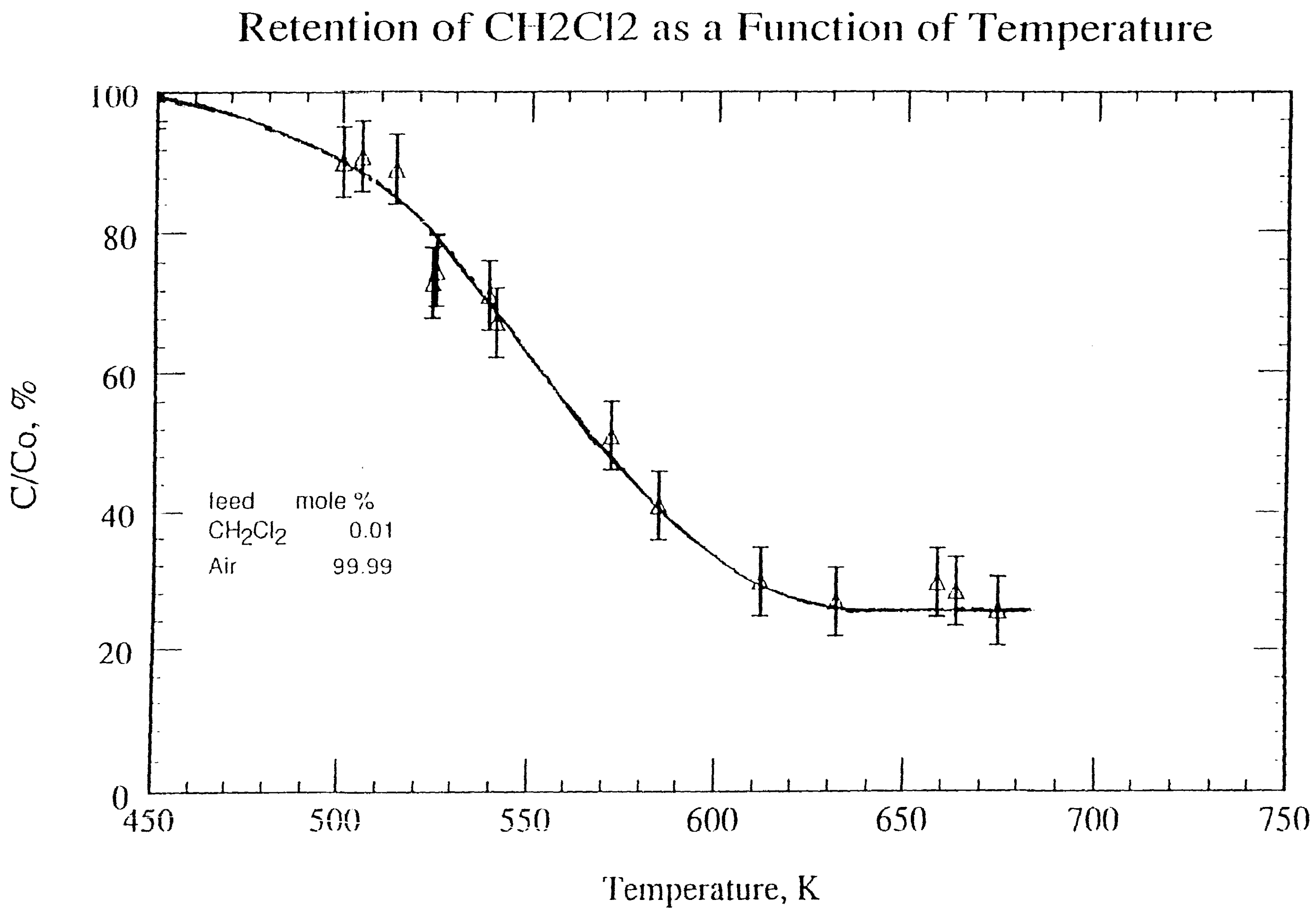
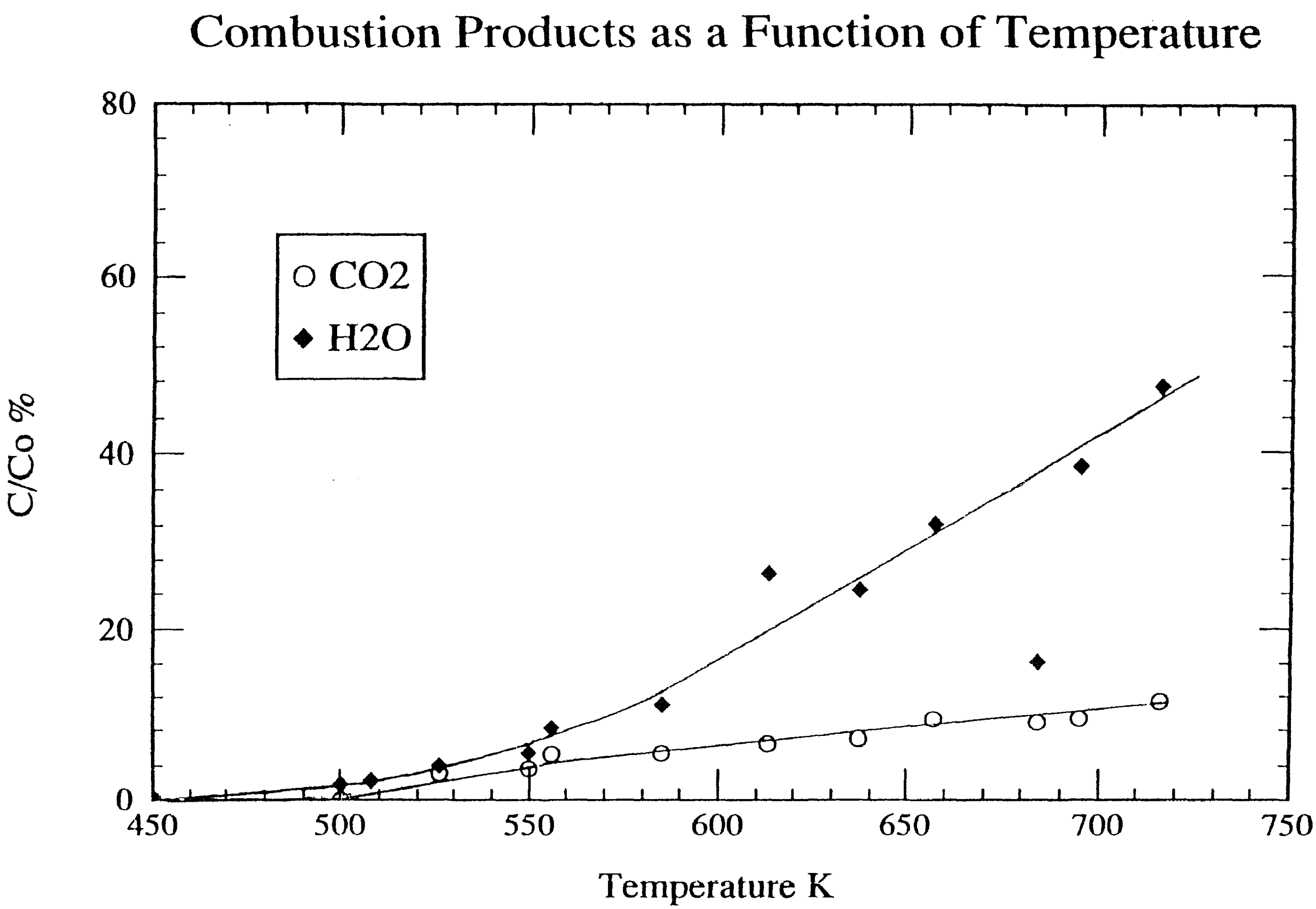


Figure 13. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 1.67 v/v/sec

sensitive to temperature from 610 to 650 K than at temperatures lower than 610 K. At 1.67 v/v/sec, retention varied more slowly from 570 to 650 K than below this temperature range. Product distributions of chloroform, carbon tetrachloride, and water are measures of the same phenomena with temperature in the ranges of 610-650 K at 2.22 v/v/sec, and 570-625 K at 1.67 v/v/sec. The retention of dichloromethane at a space velocity of 1.67 v/v/sec became independent of temperature over 625 K. Products chloroform, carbon tetrachloride and water also followed this trend, becoming fairly constant above 625 K. Carbon dioxide and hydrogen chloride increased linearly through the whole experimental temperature range. Product concentration distributions at 6.67, 2.22, 1.67 v/v/sec are shown in Figures 14, 15, 16, 17, 18 and 19, and at 3.33 v/v/sec are shown in Figures 9 and 10.

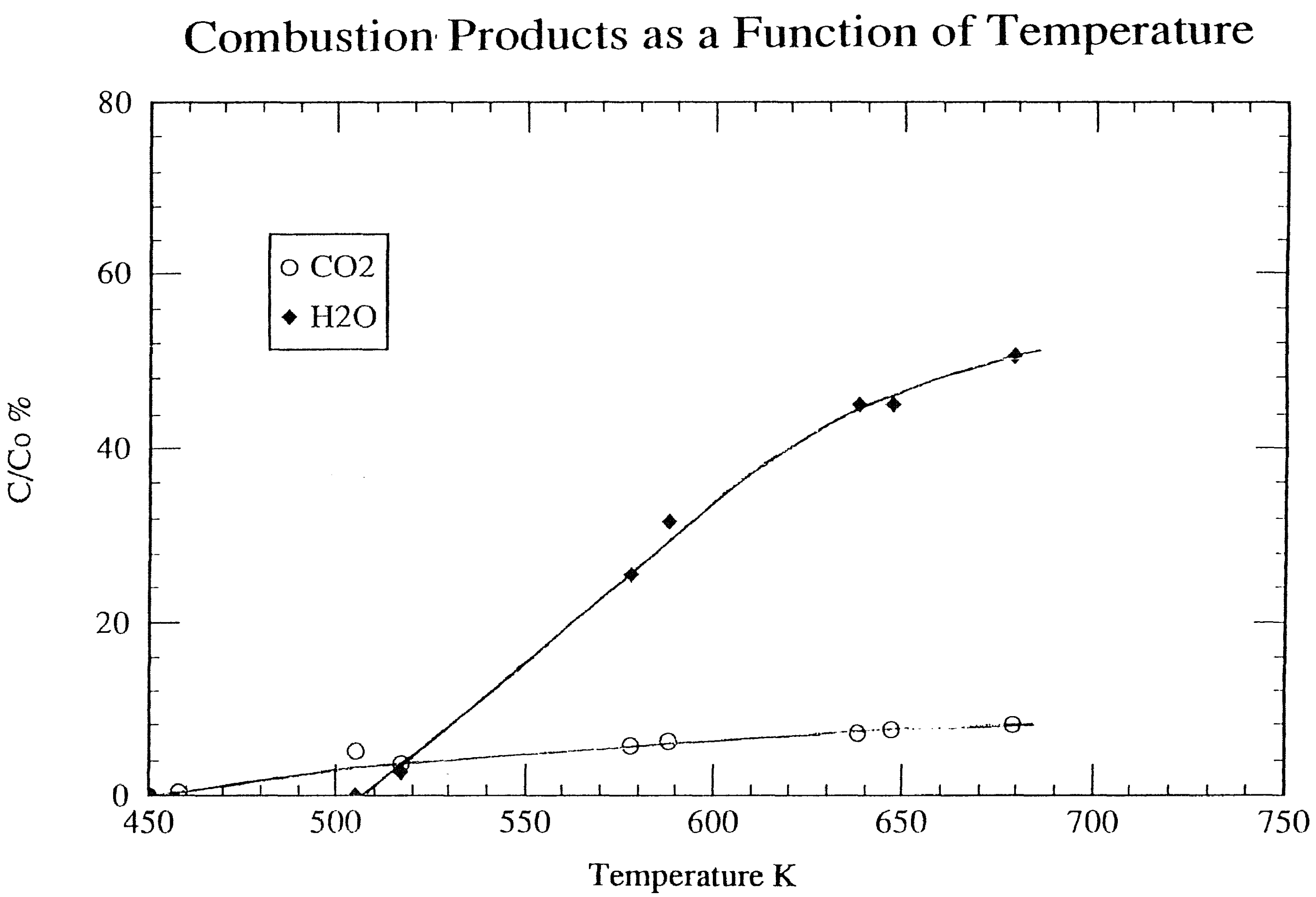
2. Methane Effect on Reaction

In order to study the effect of an added fuel, a feed composed of 2.33 % methane, 0.01 % dichloromethane and 96.77 % mole fraction of air was run experimentally. Table 8 summarizes the data obtained from the air oxidation of dichloromethane in the presence of methane at 3.33 v/v/sec over 0.4 g of MnO_2 catalyst. The experimental results indicate that the light-off temperature is on the order of 500 K. At higher temperatures, the conversion of dichloromethane and concentration of products water and chloroform increased with temperature. Carbon tetrachloride was obtained at the highest temperatures.



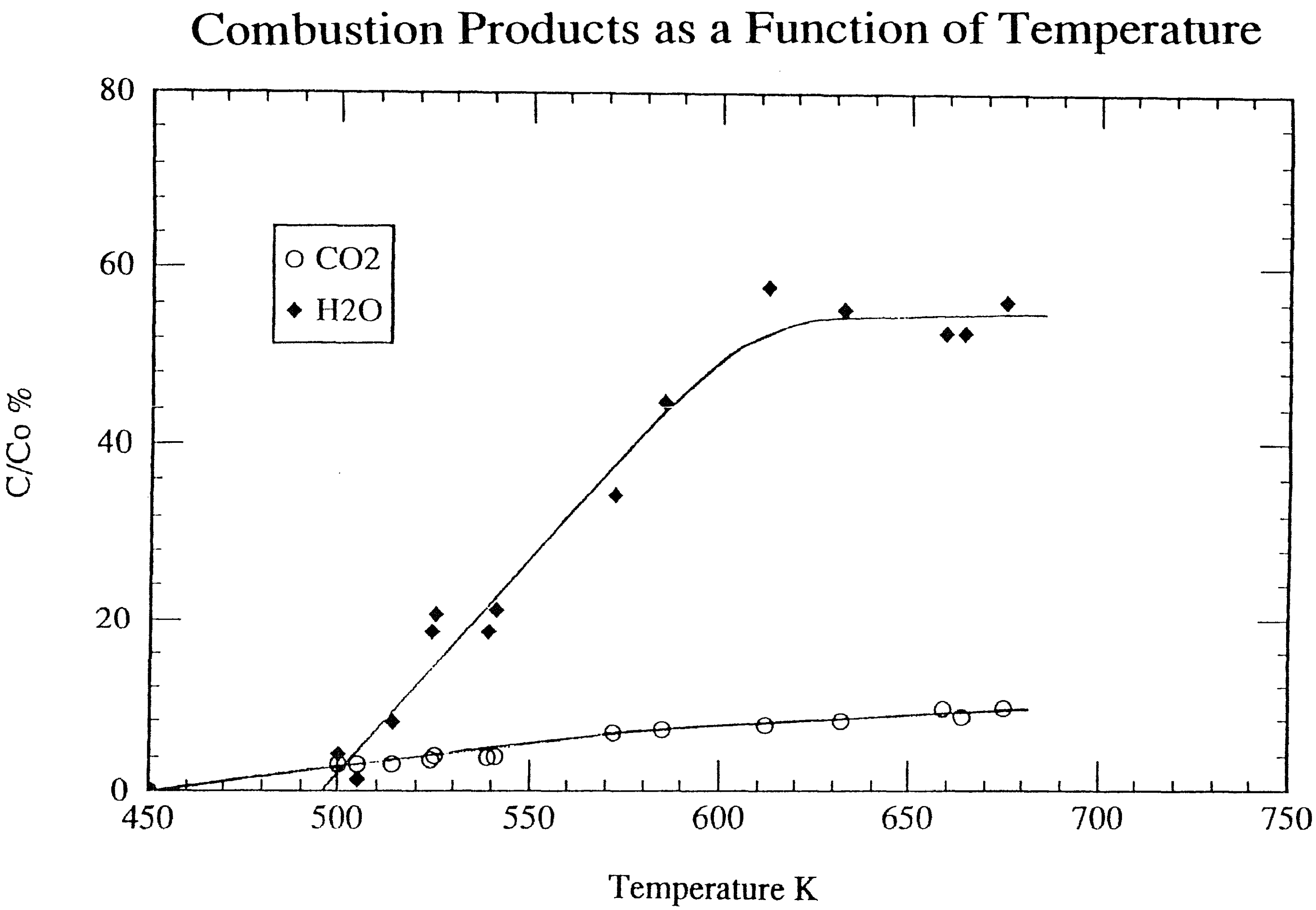
Co is the initial concentration of CH_2Cl_2 at CH_2Cl_2 and air

Figure 14. Combustion products as a function of temperature at a space velocity of 6.67 v/v/sec



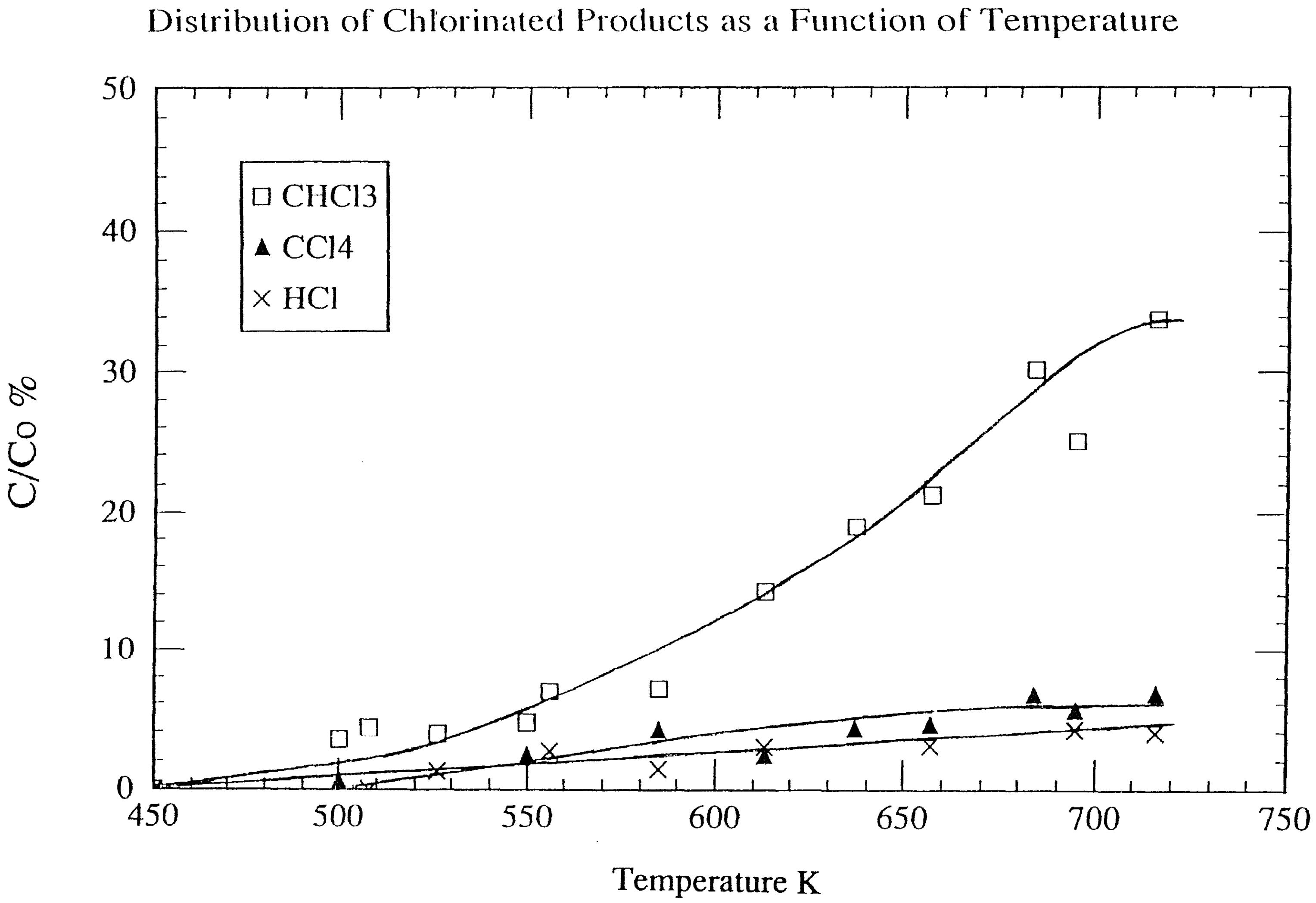
Co is the initial concentration at CH2Cl2+air

Figure 15. Combustion products as a function of temperature at a space velocity of 2.22 v/v/sec



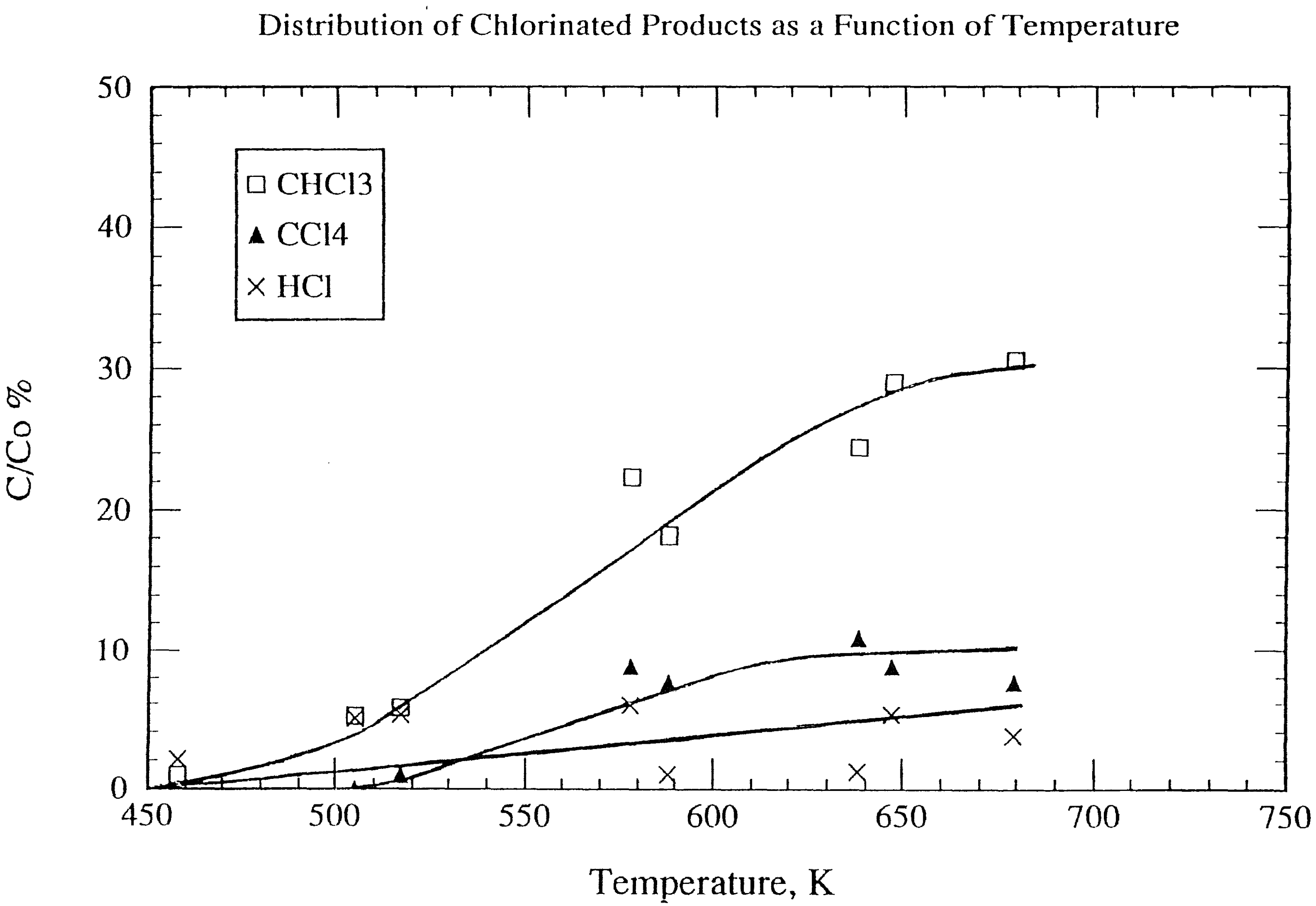
Co is the initial concentration at CH2Cl2+air

Figure 16. Combustion products as a function of temperature at a space velocity of 1.67 v/v/sec



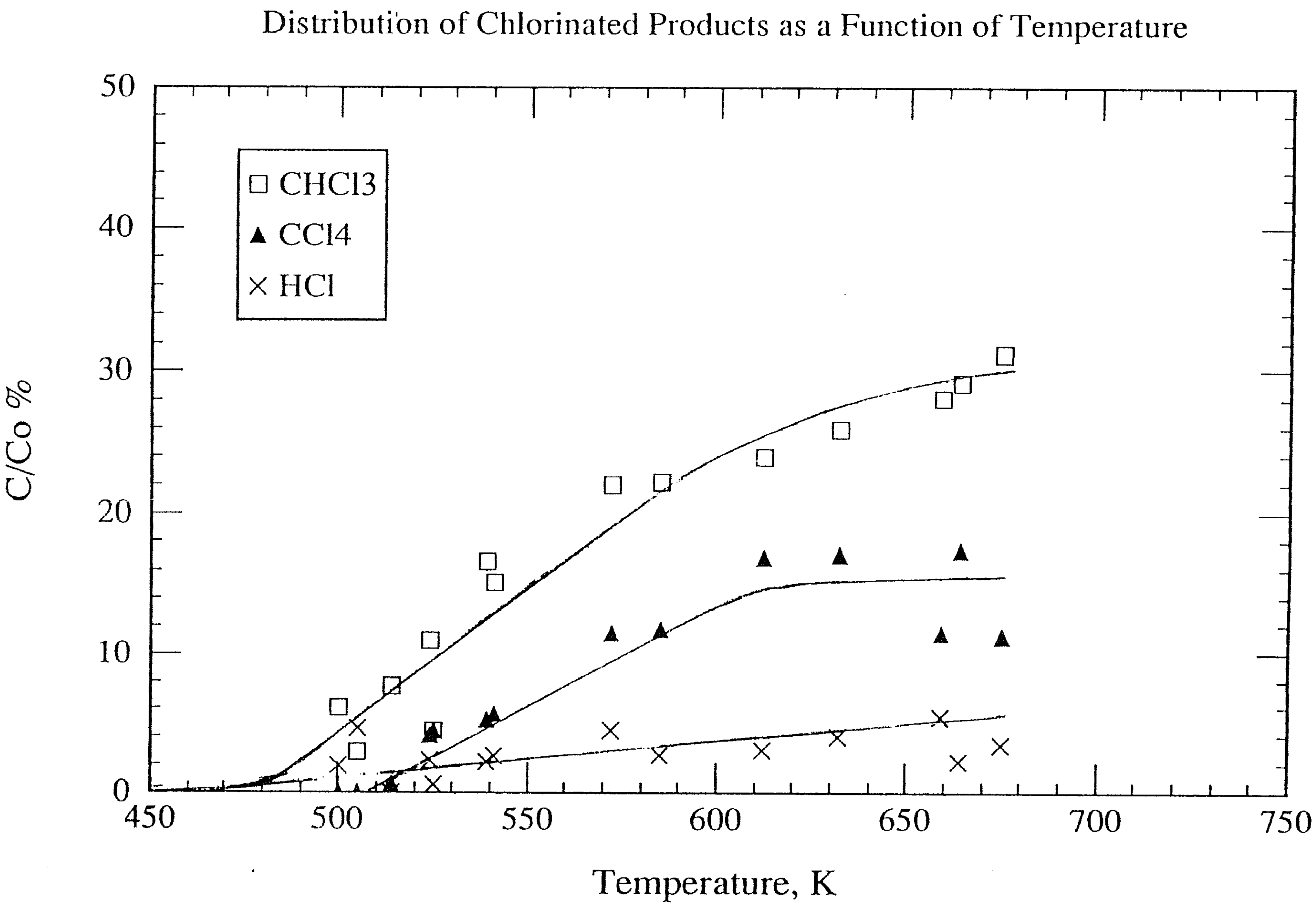
Co is the initial concentration of CH2Cl2 at CH2Cl2 + air

Figure 17. Distribution of chlorinated products as a function of temperature at a space velocity of 6.67 v/v/sec



Co is the initial concentration of CH2Cl2 at CH2Cl2 + air

Figure 18. Distribution of chlorinated products as a function of temperature at a space velocity of 2.22 v/v/sec



Distribution of Chlorinated Products as a Function of Temperature

Co is the initial concentration of CH2Cl2 at CH2Cl2 + air

Figure 19. Distribution of chlorinated products as a function of temperature at a space velocity of 1.67 v/v/sec

TABLE 8 OXIDATION OF DICHLOROMETHANE WITH AIR IN THE PRESENCE OF METHANE AT A SPACE VELOCITY OF 3.33 v/v/sec AND 0.4 g OF MnO_2 CATALYST

Temp K	Concentration of C/Co %							Material Balance	
	CO_2	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3Cl	HCl	H_2O	Cl	C
450	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
501	0.0	94.6	1.7			2.9	3.1	99	96
529	2.0	90.1	4.3			3.5	6.0	98	96
566	4.1	84.3	8.7	1.1		2.8	9.9	102	98
568	4.4	78.3	10.4			4.1	19.1	96	93
573	4.6	72.2	13.0	2.4	0.03	3.6	24.2	96	92
603	5.0	64.2	17.0	4.9		4.0	25.3	103	91
605	6.0	63.0	18.9	5.1	0.05	5.2	27.5	104	93
613	6.7	65.5	21.6	7.7	1.3	2.0	21.7	114	103
648	7.5	46.4	22.9	9.8	1.2	5.5	40.4	103	88
660	7.7	41.8	23.7	10.0	2.0	6.4	43.4	102	85
664	9.2	41.2	25.0	10.0	2.7	6.6	39.0	103	88
683	9.8	42.0	24.5	8.5	6.1	7.0	33.1	99	91
705	10.5	40.2	28.3	7.5	4.7	7.2	35.0	104	91
721	11.8	41.6	26.2	5.8	5.9	8.0	32.5	100	91
722	11.8	38.6	30.5	7.3	5.8	7.3	33.8	105	94

Note: Co is initial concentration of dichloromethane at atmospheric pressure.

The conversion of dichloromethane becomes a weak function of temperature above 625 K. The concentration of carbon tetrachloride had a maximum value in the range of 640-660 K. Chloromethane production increased rapidly after 660 K. The conversion of the reactant and the concentrations of products water, chloromethane, chloroform, and carbon tetrachloride were independent of temperature above 675 K. The retention of dichlormethane as a function of temperature is depicted in Figure 20. Plots of temperature vs., product concentration of chlorinated compounds, carbon dioxide, and water are shown in Figures 21 and 22.

3. Other Experimental Results

Table 9 shows that the results of the conversion of dichloromethane and concentrations of products chloroform, carbon tetrachloride from the dichloromethane, methane and air system at three space velocities (1.4, 2.5 and 4.5 v/v/sec). These runs were made at atmospheric pressure and at temperatures 583, 613 and 643 K. At 643 K, the conversion of dichloromethane changed slightly with space velocity. But at 613 K and a space velocity of 2.5 v/v/sec, results of conversion and product distribution are inconsistent with the rest of the table. This run was not rechecked. When running only methane and air at temperatures from 450 to 750 K, no reaction was observed. The conversion of dichloromethane for runs with 0.105 g of MnO_2 diluted with silica gel, at linear velocity 1.83 cm/sec , and at temperatures from 450 to 750 K is shown in Figure 23. It was found that the light-off temperature was about 550 K. The

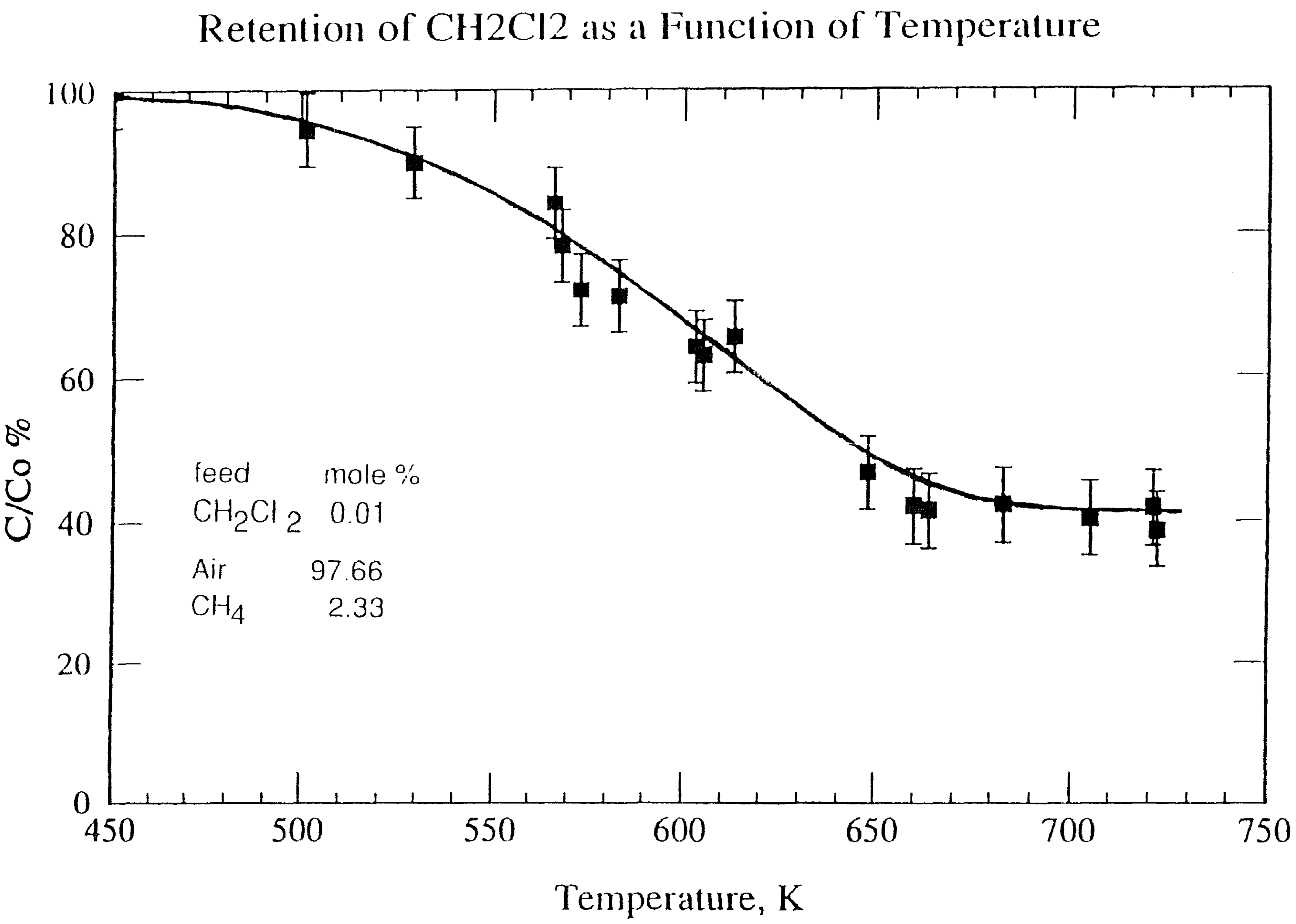
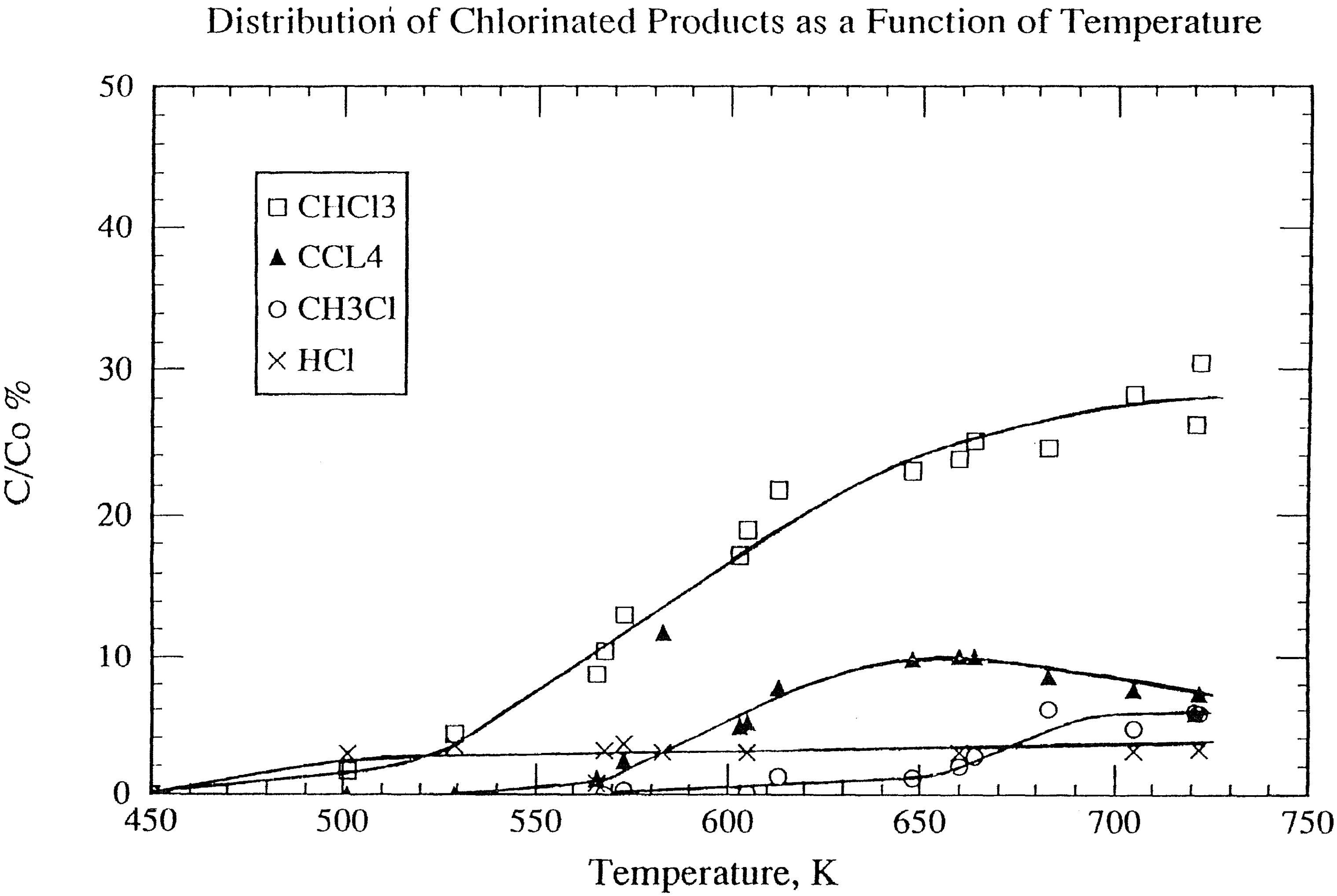
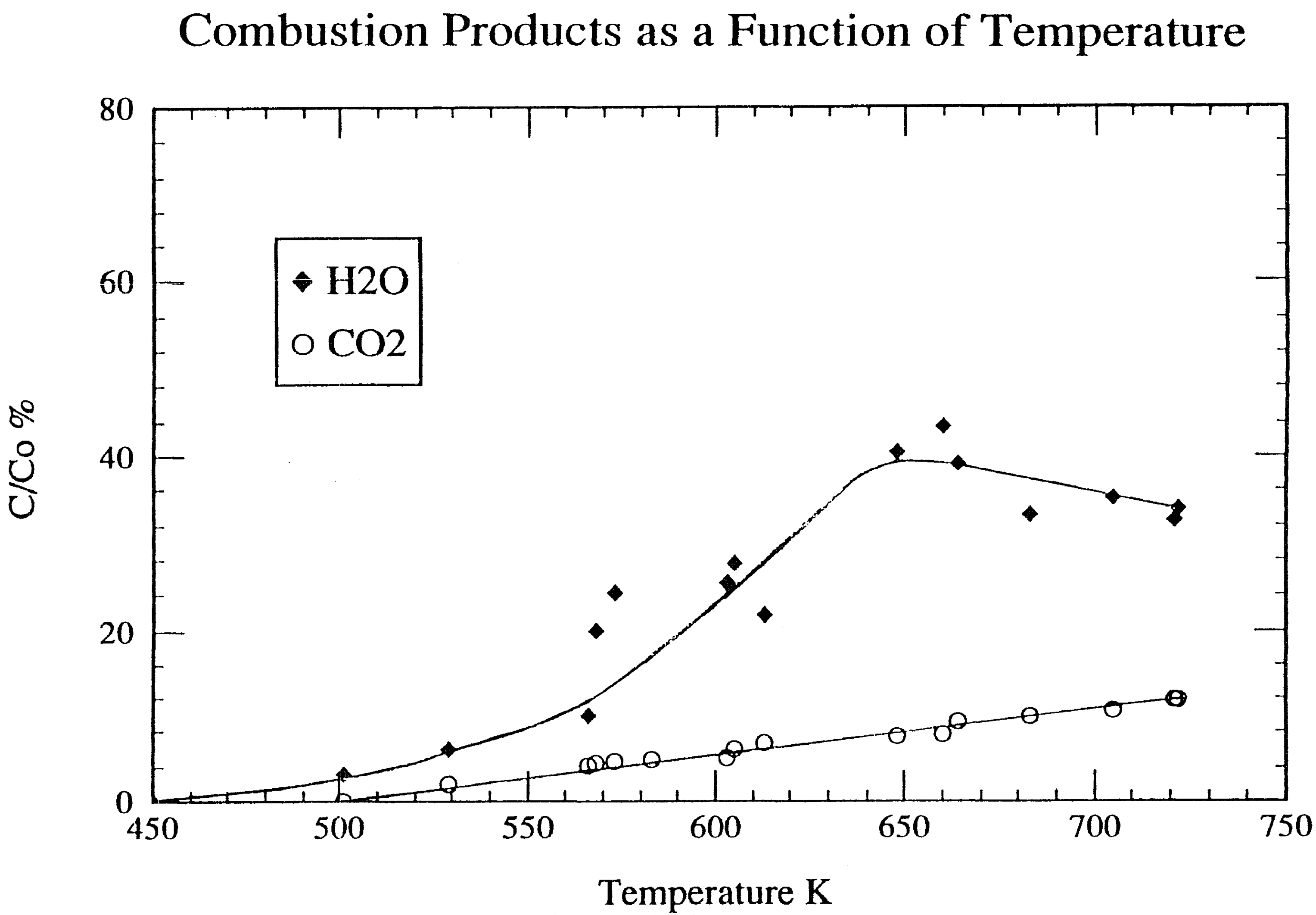


Figure 20. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 3.33 v/v/sec



Co is the initial concentration of CH2Cl2 at CH2Cl2+CH4+air

Figure 21. Distribution of chloinated products as a function of temperature at a space velocity of 3.33 v/v/sec



Co is the initial concentration of CH2Cl2 at CH2Cl2+CH4+air

Figure 22. Combustion products as a function of temperature at a space velocity of 3.33 v/v/sec

TABLE 9 SPACE VELOCITY EFFECT ON REACTIVITY AND SELECTIVITY

Temp. K	Space Velocity (v/v/sec)	CH_2Cl_2 Conversion %	$CHCl_3$ C/Co %	CCl_4 C/Co %
583	1.4	28.7	14.3	11.7
	2.5	14.8	13.3	2.5
	4.5	1.13	12.9	2.6
613	1.4	35.4	13.7	4.4
	2.5	41.7	14.8	4.9
	4.5	24.3	13.6	4.0
643	1.4	29.7	28.6	9.6
	2.5	28.4	18.8	6.3
	4.5	30.7	24.8	8.7

Note: The feed mixture was CH_2Cl_2 (0.01 mol percent), CH_4 (2.33 mol percent), and air (99.66 mol percent) over 0.4 g of catalyst MnO_2.

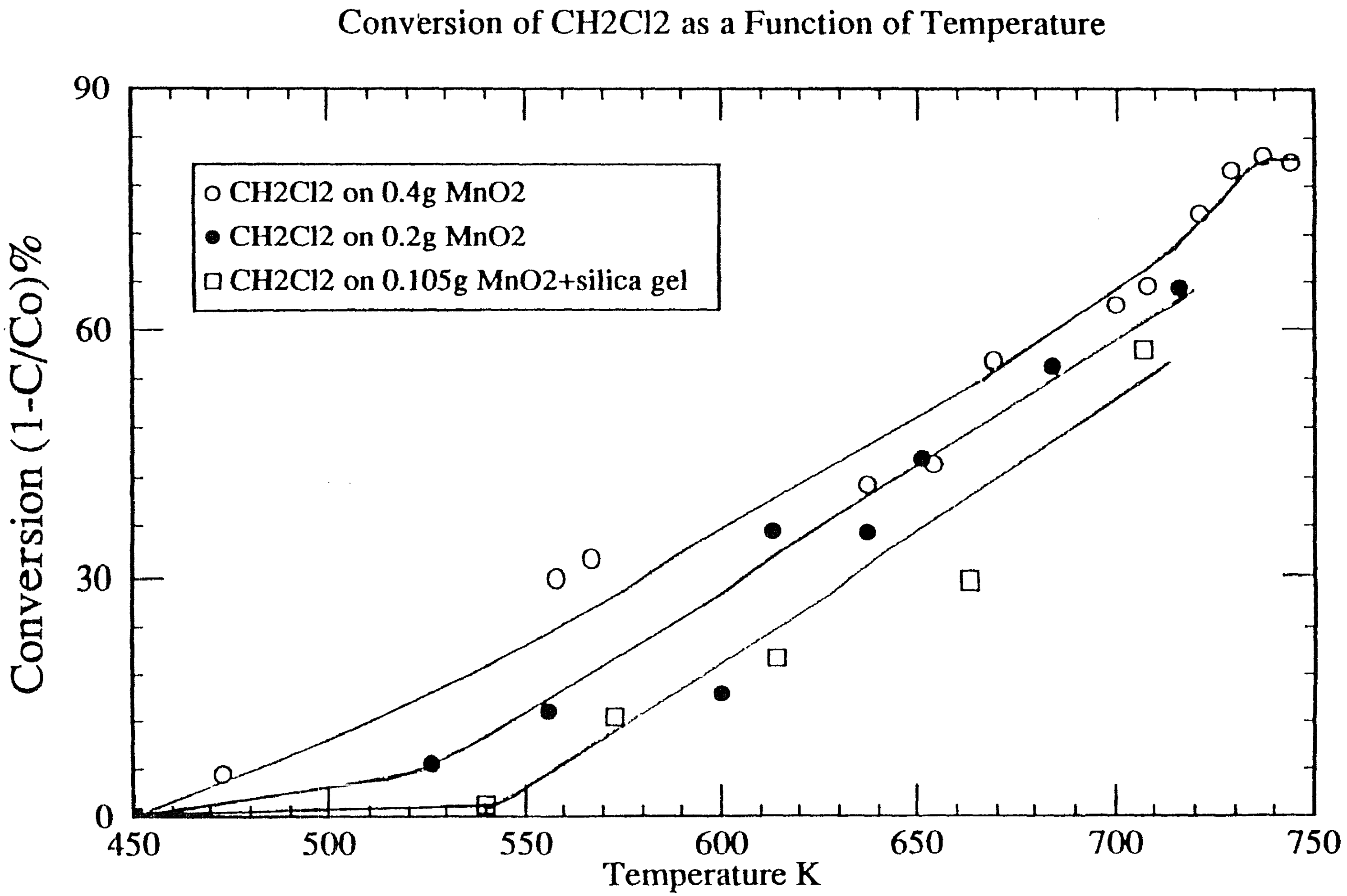


Figure 23. Conversion of CH_2Cl_2
as a function of temperature

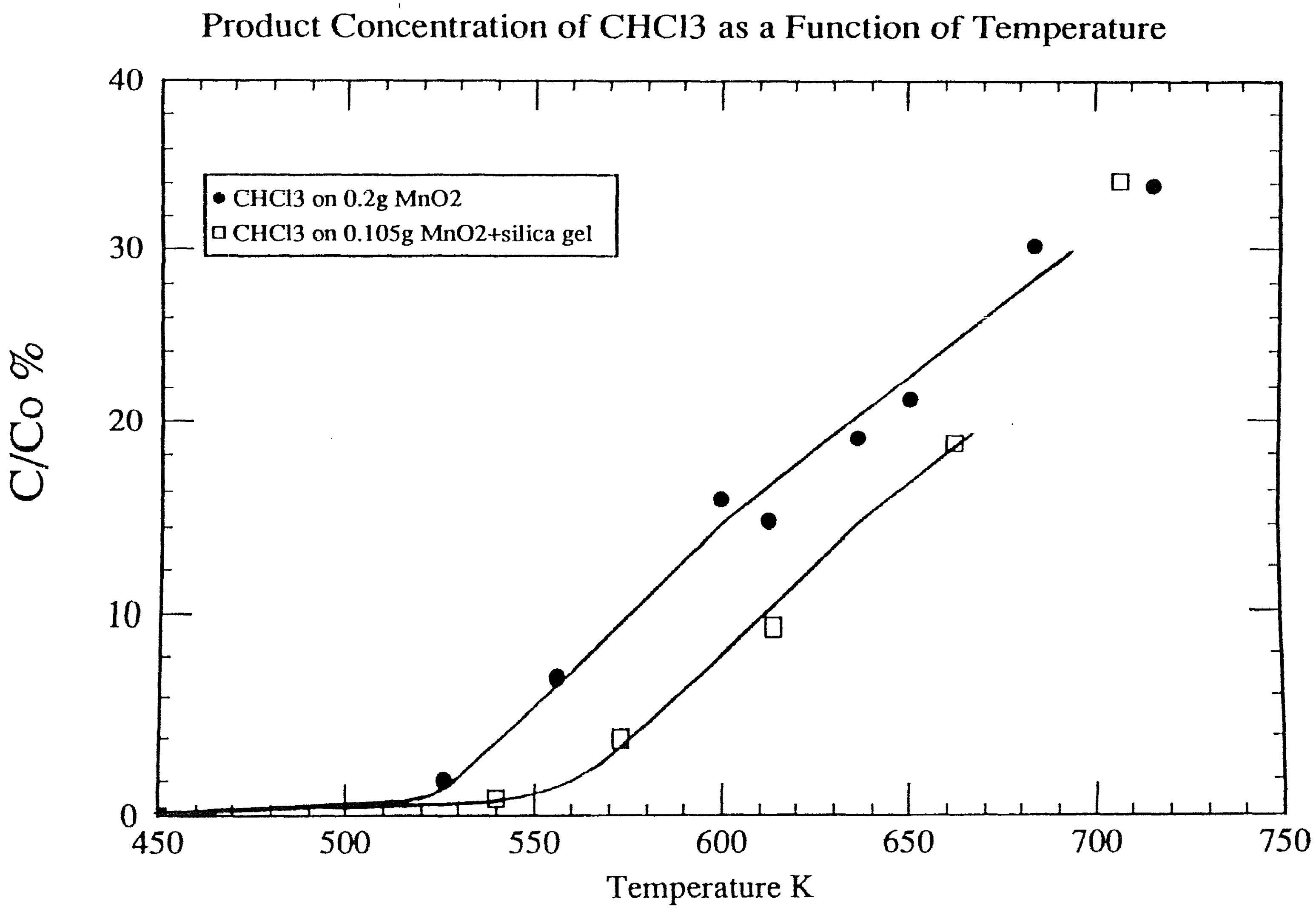


Figure 24. Product concentration of $CHCl_3$ as a function of temperature

concentration of product chloroform as a function of temperature is shown in Figure 24.

No thermal reaction of dichloromethane and air at linear velocity 1.83 cm/sec was observed at 550 K. Similarly, no reaction was observed in the temperature range of 450-750 K when dichloromethane and nitrogen were passed over 0.4 g catalyst MnO_2 at a space velocity of 3.33 v/v/sec.

DISCUSSION

A. Temperature Effect on Reactivity and Selectivity

From the experimental results, it was found that the reactivity depends on temperature. The results shows the light-off temperature is on the order of 500 K at space velocity of 3.33 v/v/sec for the CH_2Cl_2/air system and the conversion of dichloromethane was most sensitive to temperatures between 513 and 625 K, while the conversion was the least sensitive to temperature above 700 K. This suggests that a chemical kinetics controlled zone existed in the temperatures 513-625 K, while a mass controlled limited zone occurs at temperatures over 700 K. There appear to be two regimes for the destruction of dichloromethane over MnO_2: surface chemical kinetics, and bulk mass transfer. The same phenomena appear to be operating in Figures 11, 12 and 13. Temperature is a important parameter for product distribution. Figures 9 and 10 show that the concentrations of water and chloroform increased substantially as temperature increased over 513 K. Carbon tetrachloride was produced above 550 K. The effect of temperature was less pronounced on the concentrations of carbon dioxide and hydrogen chloride which agrees with the result of chemical equilibrium calculations. In addition, Table 10 shows that for temperature above 750 K, the catalyst bed pressure (P was measured by a pressure manometer upstream and downstream of the bed) sharply drops from 75 psia to 25 psia. This results in a change in conversion of dichloromethane from

60-80 percent to 30-40 percent, and implies that the MnO_2 catalyst powder may undergo physical sintering and/or may have thermal cracking or phase fusion to form channels, which allowed the reactant to bypass part of catalyst.

TABLE 10 CONVERSION OF DICHLOROMETHANE VERSUS PRESSURE DROP THROUGH THE PACKED CATALYST BED

Temperature K	Pressure Drop psia	Conversion %
450	25	0.0
473	25	5.3
558	30	29.7
567	30	31.8
637	40	40.8
654	53	43.4
669	62	56.2
700	65	63.1
708	69	65.5
721	71	74.6
729	73	80.8
737	75	81.8
744	75	81.0
756	25	41.0
763	25	32.1

Note: The feed mixture was CH_2Cl_2 with air at a space velocity 3.33 v/v/sec and 0.4 g of MnO_2 catalyst.

B. Methane Effect on Reactivity and Selectivity

Figure 25 shows how retention of dichloromethane compares in the air only system with the methane and air system as a function of temperature. The mass transfer controlled zone with methane appears to occur at lower temperature (675 K in Figure 20) than in the system without methane (700 K in figure 8). It is not clear whether this result is due to experimental scatter or a more fundamental reason. One such reason could be the larger molecular crossection for methane compared with air. Conversion of dichloromethane in both systems was not significantly different in the temperatures range of 513-625 K. Furthermore, running only methane and air through the catalyst bed in the 450-750 K temperature range showed that no reaction occurs. Consequently, methane is probably not involved in the decomposition of dichloromethane. However, from Figure 21, it is clear that the product distribution of chlorine compounds had changed. Chloromethane is detected at about 575 K. In the temperature range of 625-675 K, chloromethane and chloroform kept increasing, whereas carbon tetrachloride appeared constant or decreased slightly. At temperatures over 675 K, the concentrations of chloromethane, chloroform and carbon tetrachloride became constant, which indicates that the reaction became controlled by bulk mass transfer. It suggests that the global reaction of methane with carbon tetrachloride may take place on the catalyst surface, forming products as follow:

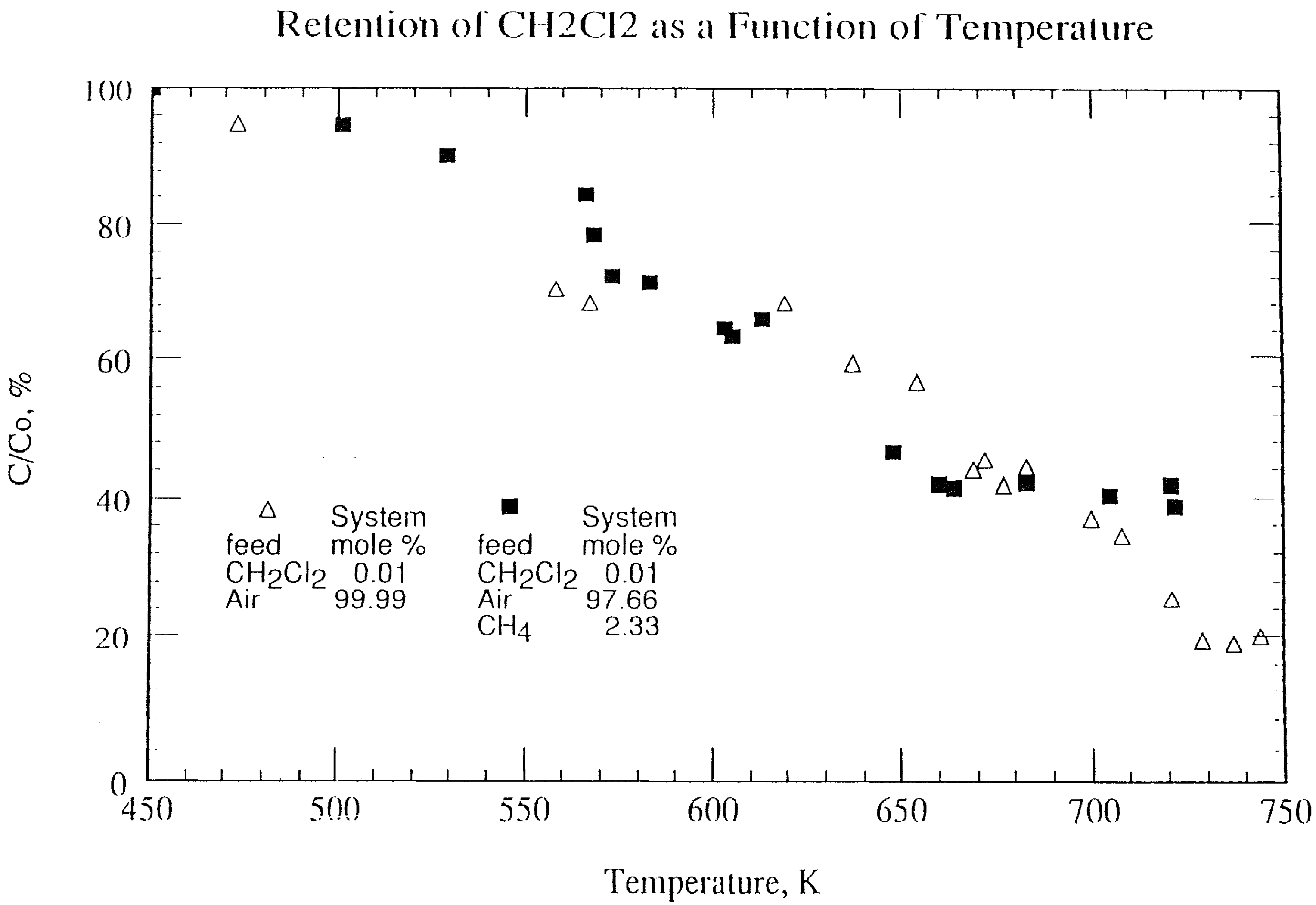


Figure 25. Retention of CH_2Cl_2 as a function of temperature at a space velocity of 3.33 v/v/sec

$$CH_4 + CCl_4 \text{ ------> } CH_3Cl + CHCl_3 \qquad (4-1)$$

The product CH_3Cl is only found when methane is present adding credibility to this reaction. Unfortunately, since methane concentration was much larger than dichloromethane, and was also much larger than carbon tetrachloride, reaction (4-1) cannot be verified. On the other hand, Figures 21 and 22 show that carbon dioxide, water and hydrogen chloride product distributions do not change when methane is present. So one can assume that methane's function was as a source of hydrogen. This is in contrast to chemical equilibrium predictions that show water increases in the system with methane because methane decomposes to carbon dioxide and water as illustrated in Table 6 and Figure 7.

C. Residence Time Effect on Reactivity and Selectivity

The effect of residence time (space velocity)$^{-1}$ at constant linear velocity (1.83 cm/sec) and equivalent temperatures shows that increased residence time (decreased space velocity) increased dichloromethane conversion. This is illustrated in Figures 8, 11, 12 and 13. Higher reaction rate are therefore obtained at the same temperature. Lower light-off temperatures were measured for higher residence times and the diffusion and mass transfer controlled regions also occurred at lower temperatures. Clearly, conversion of dichloromethane is a strong function of residence time at the same linear velocity.

It was also found that chlorocarbon products varied with changing residence time. Figures 10, 17, 18 and 19 show that the ratio of concentration of chloroform to carbon tetrachloride decreased as residence time increased, which suggests that if dichloromethane stays in the catalyst bed for a relatively long time, where it reacts to form more highly chlorinated compounds such as carbon tetrachloride. However, Figures 9, 14, 15 and 16 show that carbon dioxide is not affected by residence time. At constant temperature, water production increases with residence time (space velocity decreases). At higher residence times, water production becomes independent of temperature above about 650 K.

D. Operating Conditions Effect on the Reaction

Figure 23 shows that at the same temperatures, decomposition rate of dichloromethane on 0.4 g of catalyst was higher than 0.2 g of catalyst which was higher than on 0.105 g of catalyst (diluted with silica gel to the same volume). This indicates that the reactivity is affected by the active charge of MnO_2 catalyst. The curve for conversion versus temperature in the 0.105 g MnO_2 diluted with silica gel case were parallel to the 0.2 g and 0.4 g of MnO_2 curves, which clearly indicates that the presence of additional catalytic material in the certain ranges allowed the light-off temperature to take place a lower temperature (510 vs., 550 K in Figure 23), but it did not change the characteristics of the catalyst since all three curves had the same shape. One can further see that the apparent rate of reaction (slope of the linear portion of the curve) is independent of catalyst active charge change at the same flow rate. Furthermore, the same response was found for chlorinated compound chloroform which is depicted in Figure 24.

On the other hand, at different space velocities, linear velocities and 0.4 g MnO_2, Table 9 shows that the conversion of dichloromethane and the concentrations of products chloroform and carbon tetrachloride decreased as space velocity increased at 513 K. However, at temperature 643 K, the conversion of dichloromethane and the concentration of all chlorinated products except for hydrogen chloride tended to remain constant when space velocity was varied.

In addition, using a non-oxygen containing carrier gas (nitrogen) to replace air, no reaction was observed even at a temperature as high as 750 K.

E. Chemical Reaction Kinetics

In this study, air (O_2+3.78 N_2) was used as the carrier gas and was in very large excess. The mole fraction of CH_2Cl_2 employed for all the temperature studies was 100 ppm. It is reasonable to assume that the reaction process would be pseudo first order because of the large excess O_2

$$CH_2Cl_2+O_2 \text{ (excess)} \rightarrow CO_2+H_2O+HCl+CHCl_3+CCl_4 \qquad (4-2)$$

(not mass balanced)

then from chemical kinetics:

$$-\,dC/dt = k[C] \qquad (4-3)$$

where C is the concentration of the reactant;

k is the rate constant;

t is residence time.

Solving equation (4-3) over limits t = 0 at C = Co, we obtain

$$\ln(Co/C) = kt \tag{4-4}$$

where Co is initial concentration of dichloromethane;

C is the concentration of dichlormethane as a function of residence time.

According to the Arrhenius equation, the rate constant also can be described as follow:

$$k = A \exp(-E/RT) \tag{2-4}$$

where A is the pre-exponential factor;

E is activation energy.

then,

$$\ln k = \ln A - E/RT \tag{2-5}$$

For the system of CH_2Cl_2 and air, using equation (4-4), a plot of ln Co/C vs., t can be used to obtain k from slopes, e.g., Figure 26. These data can then be plotted according to equation (2-5), e.g., plot ln k vs., 1/T, to obtain E, A as indicated in Figure 27.

An approximate equation for the reactions of CH_2Cl_2+CH_4+air system at 0.3 sec residence time (3.33 v/v/sec) is given in equation (4-5):

$$CH_2Cl_2+CH_4+O_2\ (\text{excess}) \dashrightarrow CO_2+H_2O+HCl+CH_3Cl+CHCl_3+CCl_4 \tag{4-5}$$

also we have:

$$-\,dC/dt = k\,[C_{CH2Cl2}]\,[C_{CH4}] \tag{4-6}$$

Equation (4-6) can be simplified because $CH_4 >> CH_2Cl_2$

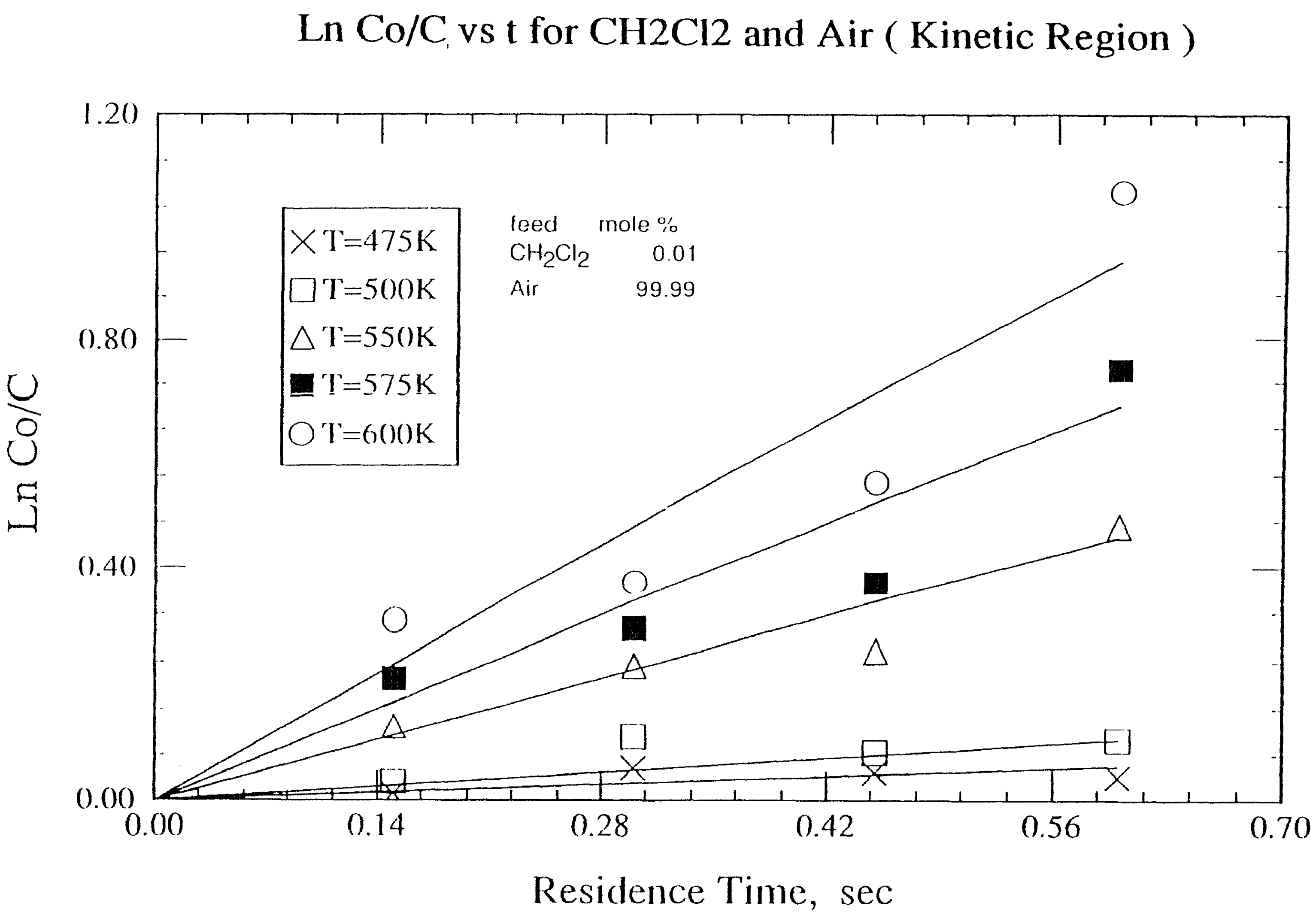


Figure 26. Ln Co/C vs t for CH_2Cl_2 and air (kinetic region)

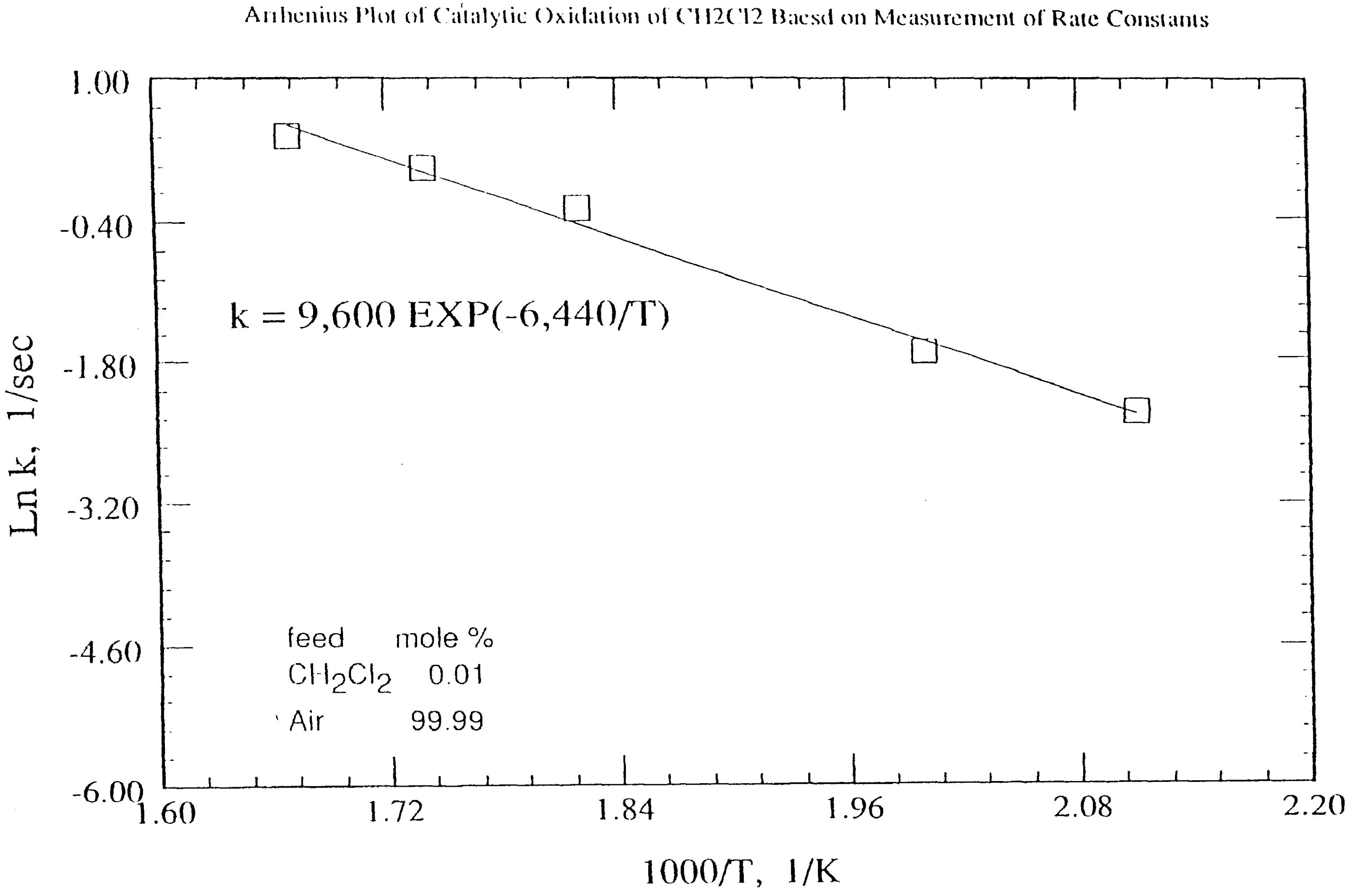


Figure 27. Arrhenius plot of catalytic oxidation of CH_2Cl_2 based on measurement of rate constants

(233:1), therefore C_{CH4} is considered constant. So equation (4-6) reduced to:

$$- dC/dt = k' \ [C_{CH2Cl2}] \qquad (4-7)$$

Which can be solved with the usual boundary conditions to:

$$\ln (Co/C) = k't \qquad (4-8)$$

Combining equations (4-8) and (2-1), one obtains:

$$\ln (Co/C) = t \ A \exp (-E/RT) \qquad (4-9)$$

Taking the natural logarithm of both sides, we obtain:

$$\ln [\ln (Co/C)] = \ln At - E/RT \qquad (4-10)$$

A plot of ln [ln (Co/C)] vs., 1/T allows us to obtain E, A as illustrated in Figure 28.

In addition, the characteristics of the diffusion limited rate constant k_D is seen to vary according to

$$k \propto T^n \qquad (2-6)$$

This is the form one would expect from the kinetic theory, where n is 1.7. Figures 29 and 30 show plots ln (Co/C) vs., t and plots ln k vs., ln T for the CH_2Cl_2 + air system. Figure 31 illustrates the results of ln [ln (Co/C)] vs., ln T for the CH_2Cl_2 + CH_4 + air system to estimate the diffusion temperature coefficient. Table 11 summarizes the final results of the kinetics analysis. These results are consistent with expected theoretical behavior.

TABLE 11 CHEMICAL KINETICS DATA

	A 1,000/sec	E kcal/mol	diffusion exponent
CH_2Cl_2+air	9.6(±0.6)	12.7(±0.2)	2.8(±0.2)
CH_2Cl_2+CH_4+air	18.8(±0.8)	11.4(±0.9)	1.6(±0.5)

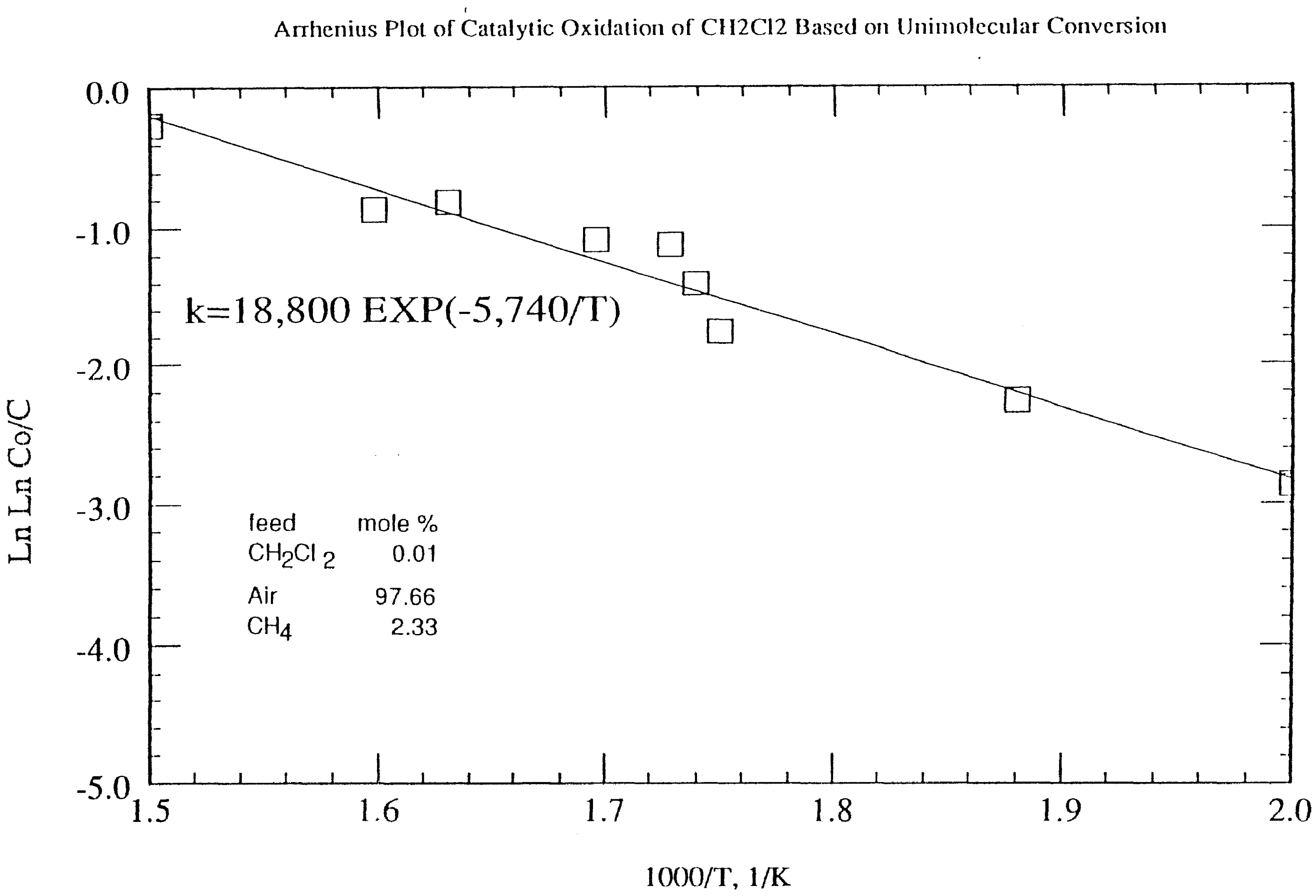


Figure 28. Arrhenius plot of catalytic oxidation of CH_2Cl_2 based on unimolecular conversion

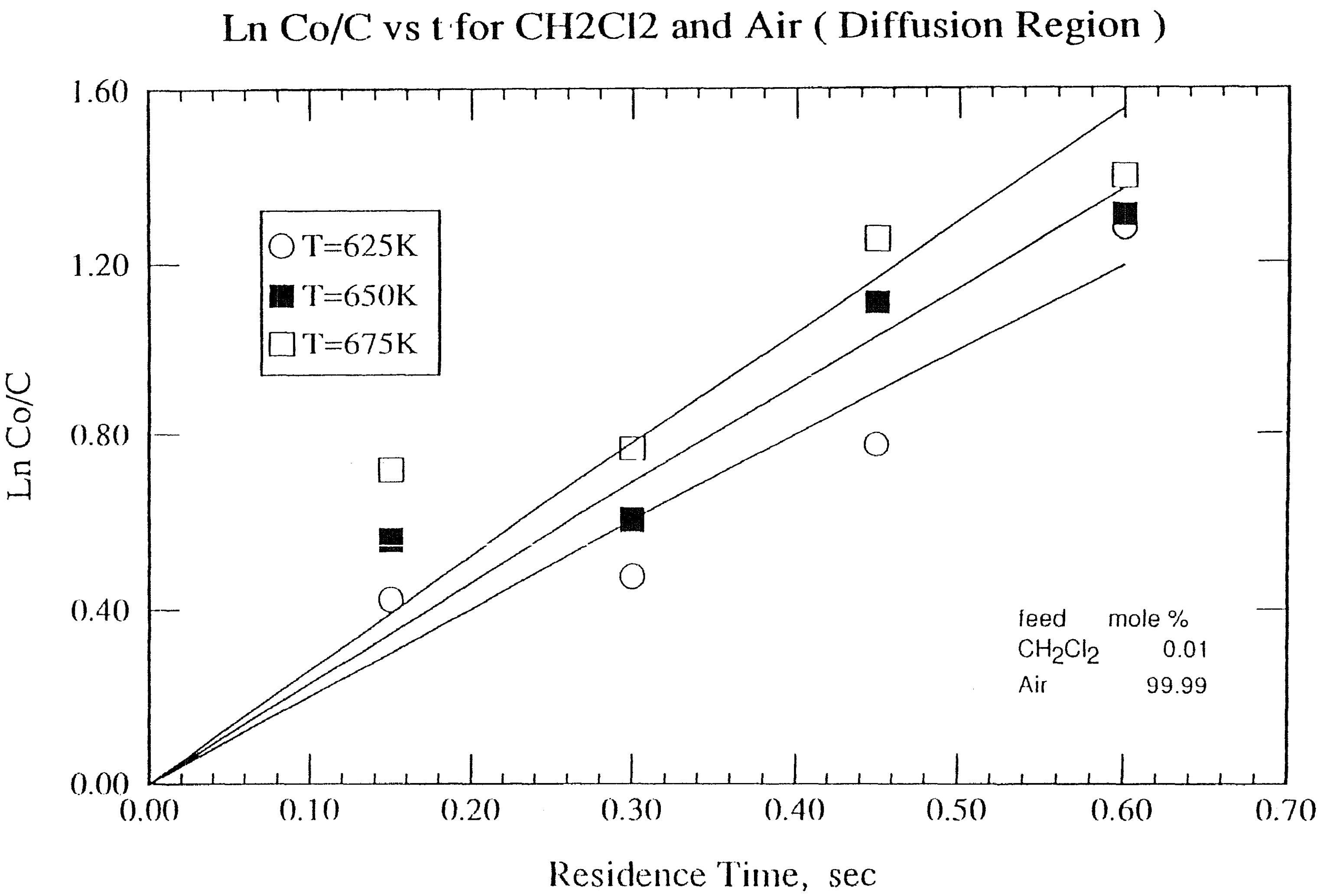


Figure 29. Ln Co/C vs t for CH_2Cl_2 and air (diffusion region)

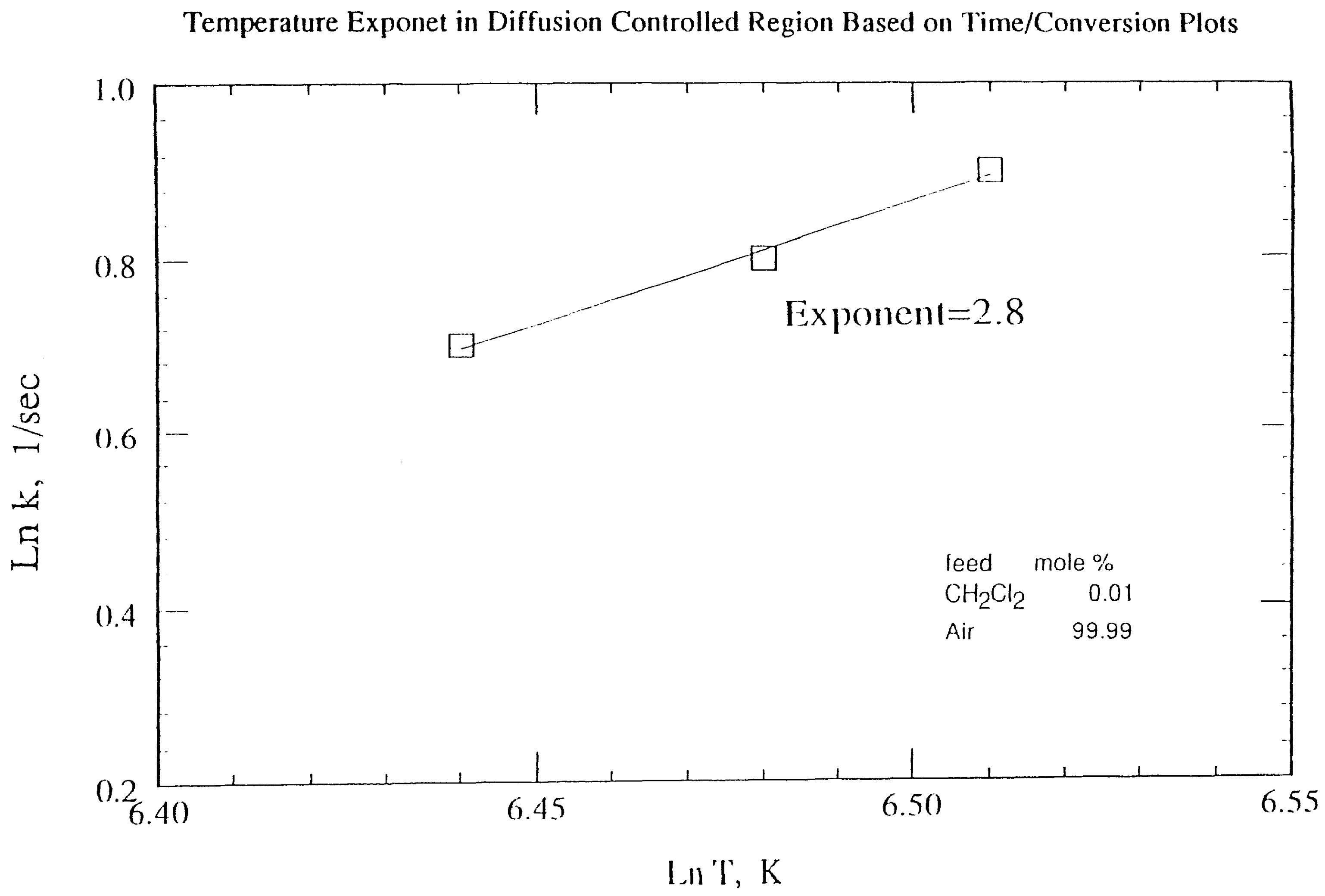


Figure 30. Temperature exponent in diffusion controlled region based on time/conversion plots

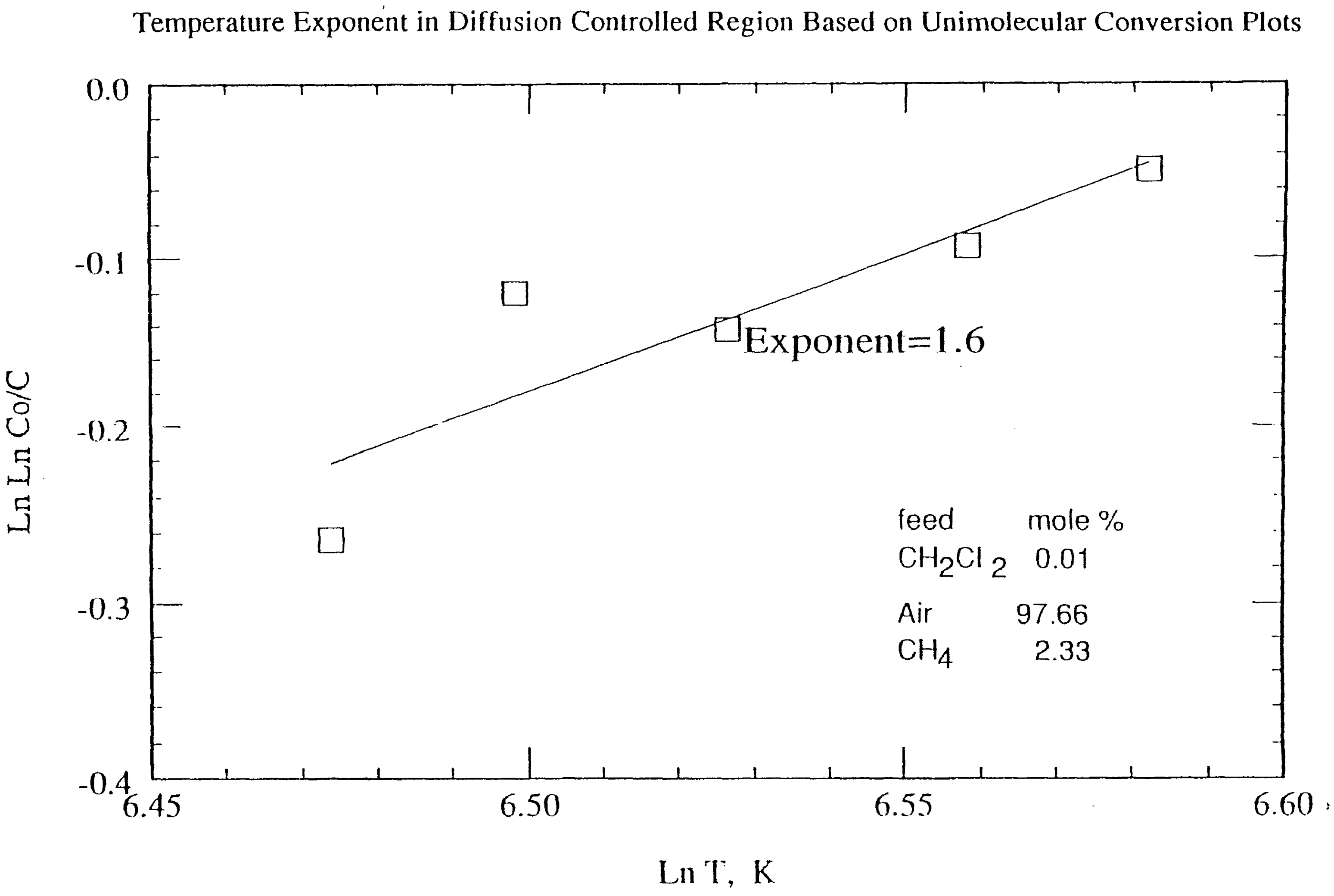


Figure 31. Temperature exponent in diffusion controlled region based on unimolecular conversion plots

Accordingly, the decomposition of dichloromethane over MnO_2 catalyst follows a path consisting of chemical kinetic control and diffusion control regions. Since the activation energies are the same, within experimental error, between the systems with methane and without methane, this demonstrates methane does not affect the rate determining step. Figure 26 shows a straight line relationship between Ln C/Co and t, which indicates that the assumption of first order reaction is realistic.

F. Reactions Involved in the Destruction of Dichloromethane

In this study, it is proposed that the decomposition of dichloromethane may involve the following global reactions on the catalyst (28):

1. $CH_2Cl_2 + O_2 \text{ ---> } CO_2 + 2\ HCl$ (4-11)
2. $4\ HCl + O_2 \text{ ----> } 2\ Cl_2 + 2\ H_2O$ (4-12)
3. $2\ CH_2Cl_2 + 2\ HCl + O_2 \text{ ---> } 2\ CHCl_3 + 2\ H_2O$ (4-13)
4. $2\ CHCl_3 + 2\ HCl + O_2 \text{ ---> } 2\ CCl_4 + 2\ H_2O$ (4-14)
5. $4\ CH_2Cl_2 + Cl_2 + O_2 \text{ ---> } 4\ CCl_4 + 2\ H_2O$ (4-15)

Other reactions that may also be considered are:

6. $4\ CHCl_3 + 2\ Cl_2 \text{ ---> } 4\ CCl_4 + 2\ H_2O$ (4-16)
7. $CH_2Cl_2 + Cl_2 \text{ ---> } CHCl_3 + HCl$ (4-17)
8. $CHCl_3 + Cl_2 \text{ ---> } CCl_4 + HCl$ (4-18)

The average conversion of dichloromethane is about 50-80 percent which can be obtained from Figures 8, 11, 12 and 13. The formation of chloroform and carbon tetrachloride, as shown in Figures 10, 14, 15 and 16, are substantially around 20-30 percent, and 8-10 percent, respectively. The formation of chloroform probably occurs as a result of the reactions summarized by equations (4-12 to 4-17), and may involve oxychlorination of dichloromethane. Formation of carbon tetrachloride may follow a similar pattern to chloroform production, viz., by further oxychlorinating chloroform that had been previously formed. The residence time effect on chlorinated products ratio change can most likely be explained from equation (4-14). Also, equations (4-16 to 4-18) may explain why chlorine gas (Cl_2), a major product of chemical equilibrium calculations, was not found experimentally. From these equations, it can be easily seen that carbon dioxide remains at almost the same level as carbon tetrachloride does in Figure 9.

A sample way to rationalize the difference between experimental results and equilibrium predictions is to look at conversion as a function of time. Oxychlorination converts HCl to Cl_2 which then reacts with dichloromethane to form chloroform or further to carbon tetrachloride at a relative short residence times (higher space velocities), i.e., 0.3 sec. As residence time increases, half of all starting material could chlorinate to carbon tetrachloride and the rest would be converted to carbon dioxide and water. As residence time further increases, the only possible reaction for CCl_4 is to CO_2, Cl_2, and HCl (with the previously produced H_2O). Ultimately, at infinite residence time, the only products would be CO_2, H_2O, Cl_2 and HCl in agreement with thermodynamics.

CONCLUSIONS

1. The partial catalytic oxidation of dichloromethane over MnO_2 occurs at a much lower temperature than homogeneous thermal incineration. The light off temperature is on the order of 500 K.

2. Temperature is the most important parameter in the catalytic reaction of dichloromethane. There are two rate controlling regions based on temperature dependence in the decomposition of dichloromethane over MnO_2 catalyst: chemical kinetics controlled region and mass transfer controlled region. The chemical kinetics controlled region exists between 513 K and 625 K, where the conversion of dichloromethane and formation of chlorinated compounds, chloroform and carbon tetrachloride increase with temperature. The mass transfer controlled region occurs at temperatures over 700 K, where temperature becomes an insensitive parameter of the reaction. Also, temperature seem to be a major factor in deactivation of MnO_2 catalyst which may undergo thermal sintering and thermal cracking or phase fusion when temperatures above 750 K are used.

3. MnO_2 catalyst has high activity to decompose dichloromethane. Over 80 percent conversion of dichloromethane is achieved.

4. The activation energy for the oxidation of dichloromethane over MnO_2 catalyst is 12.7 kcal/mol, gas constant is 1.987 cal/(mol K). The overall rate constant,

$$k = 9,600\ (\pm 600)\ \exp\ [-12.7(\pm 0.2)/RT]\ \text{in } 1/\text{sec}.$$

5. When methane fuel is added to air and dichloromethane, it does not affect the conversion of dichlormethane over MnO_2 catalyst, but may provide hydrogen to convert carbon tetrachloride to chloromethane and chloroform by promoting secondary reactions.

6. Space velocity plays a very important role in the catalytic oxidation of dichloromethane. Conversion of dichloromethane increases as space velocity decreases at the same temperature. Furthermore, dichloromethane is oxidized causing oxychlorination to form a more chlorinated compound, carbon tetrachloride, particularly with increasing residence time.

7. The catalytic oxidation of dichloromethane occurs at a sufficiently low temperature to prevent production of NO_x.

8. The Deacon or oxychlorination reaction may contribute to the production of undesirable products which go to more chlorinated compounds, chloroform and carbon tetrachloride instead of carbon dioxide, water and HCl. This explains why the experimental results show siginificant amounts of chloroform and carbon tetrachloride production. However, thermodynamics does not predict the presence of these intermediate chlorocarbons. This is a consequence of not allowing the system to equilibrate. Had we run at zero space velocity, we would have obtained the predicted products.

9. The GC, infrared analyzer and titration measurements used in this study are considered acceptable to obtain product distributions from chlorinated hydrocarbon waste treatment by catalytic oxidation. This follows from having

obtained acceptable material balances of 85 to 104 percent for Cl and C. Also at the experimental confidence limit of 95 percent, the relative error of experimental data is about 5 percent.

10. Based on these results, one must conclude that manganese dioxide catalyst is not a good catalyst to destroy dichloromethane to environmentally acceptable products at the conditions of this study.

FUTURE WORK

The experimental results point to the future work for the destruction of chlorinated compounds should concentrate on catalytic materials that do not promote oxychlorination reactions. One such suggestion could be the development of a noble metal catalyst system which would be resistant to chlorine poisoning. Transition metals and oxides, such as iron and copper catalysts, tend to promote oxychlorination reaction.

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