Thermal Degradation Characteristics of Carbon Tetrachloride in Excess Hydrogen Atmosphere

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The pure compound chloromethanes; methyl chloride, methylene chloride, chloroform and carbon tetrachloride were used as a model of chlorocarbon system with Cl/H ratio to investigate thermal stability and hydrodechlorination process of carbon tetrachloride under excess hydrogen atmosphere.

The parent thermal stability on basis of temperature required for 99% destruction at 1 second reaction time was evaluated as $875^\circ C$ for CH_3Cl, $780^\circ C$ for CH_2Cl_2, $675^\circ C$ for $CHCl_3$ and $635^\circ C$ for CCl_4. Chloroform was thermally less stable than CCl_4 at fairly low temperatures ($<570^\circ C$). The decomposition of CCl_4 became more sensitive to increasing temperature, and CCl_4 was degraded easier than $CHCl_3$ at above $570^\circ C$.

The number and quantity of chlorinated products decreases with increasing temperature for the product distribution of CCl_4 decomposition reaction system. Formation of non-chlorinated hydrocarbons such as CH_4, C_2H_4 and C_2H_6 increased as the temperature rise and particularly small amount of methyl chloride was observed above $850^\circ C$ in CCl_4/H_2 reaction system. The less chlorinated products are more stable, with methyl chloride the most stable chlorocarbon in this reaction system.

Key words : Chloromethanes, Methyl chloride, Methylene chloride, Chloroform, Carbon tetrachloride, Thermal degradation, Pyrolysis, Excess hydrogen atmosphere, Thermal stability, Hydrodechlorination

1. INTRODUCTION

The incineration of chlorocarbons is generally performed in an oxygen rich environment that contains excess O_2 and N_2, in addition to the C and Cl from the halocarbon, with relatively small amounts of available hydrogen from the limiting fuel operation (Mason and Unget, 1979). One desired and thermodynamically favorable product from a chlorocarbon conversion process is HCl, providing there exists sufficient H_2 to achieve stoichiometric formation. The HO-H bond in water is, however, stronger than the H-Cl bond, O_2 rich conditions therefore limit hydrogen availability. Another way of looking at the problem is that oxygen and Cl are both competing for the available fuel hydrogen and this is one reason that chlorocarbons serve as flame inhibitors (Won and Bozzelli, 1992). The C-Cl bond is the next strongest compared with other possible chlorinated products such as Cl-Cl, N-Cl, or O-Cl bonds. Consequently, C-Cl may persist in an oxygen rich or hydrogen limited atmosphere (Chuang and Bozzelli, 1986). This is one reason why emission of toxic chlorine-containing organic products persists through an oxygen rich incineration, as carbon species are one of the more stable sinks for the chlorine. One possible method to obtain quantitative formation of HCl, as one of the desired and thermodynamically favorable products, from chlorocarbons, might be a straight forward thermal conversion of these compounds under a more reductive atmosphere of hydrogen. The chlorocarbon plus hydrogen system contains only carbon, hydrogen, and chlorine elements and expected to lead to formation of light hydrocarbon and hydrogen chloride at the high temperatures where complete reaction occurs. Here the carbon would be

converted to methane, ethane and ethylene (Won and Choi, 1995).

In this study, the pure compound chloromethanes were used as a model chlorocarbon system to investigate the thermal stability and hydrodechlorination processes of chlorocarbons with excess hydrogen. The reactions were studied in an isothermal tubular reactor at a total pressure of 1 atm with residence times of 0.3~2.0 seconds in the temperature range 525~900℃. We have examined intermediate and final product distributions and suggested major reaction pathways to form various products based on fundamental thermochemical and kinetic principles for pyrolytic chloromethane reaction with excess hydrogen.

2. MATERIALS AND METHODS

2.1 Experimental Method

The thermal reaction of pure compound chloromethanes in excess hydrogen reaction environment has been conducted in an isothermal tubular reactor at 1 atm total pressure. The thermal degradation products of the chloromethane in hydrogen were analyzed systematically by varying the temperature, residence time. Decomposition and reaction products were observed over temperature range 525~900℃ and residence times of 0.3~2.0 seconds.

A diagram of the experimental system is shown in Figure 1. Hydrogen gas was passed through a multi-saturator train held at 0℃ to insure saturation with chlromethane at a constant reference temperature for accurate vapor pressure calculation. A second (dilutent) stream of hydrogen gas was used to achieve the desired mole fraction of chloromethane (4%) that was maintained through whole experiment. The reagent with hydrogen gas was fed continuously into tubular flow reactor in vapor phase. The mixture was preheated to about 200℃ before entering the reactor to improve isothermal temperature control. The reactor effluent was passed through heated transfer lines to the GC sampling valves and exhaust. All gas lines to the analytical equipment were held at 170℃ to limit conden-
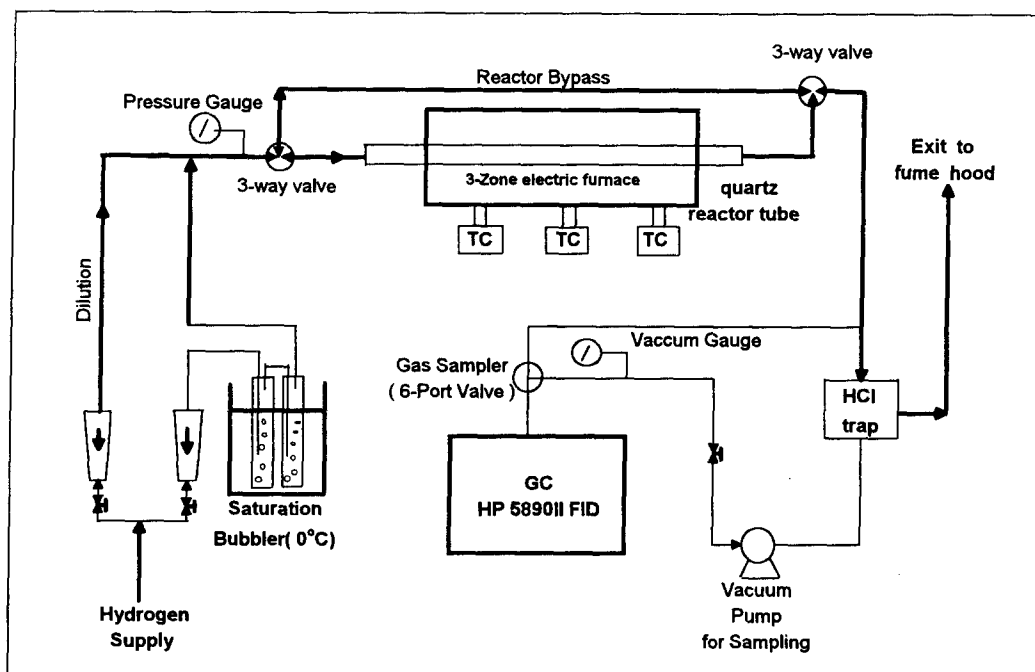

Fig. 1. Schematic diagram of experimental apparatus.

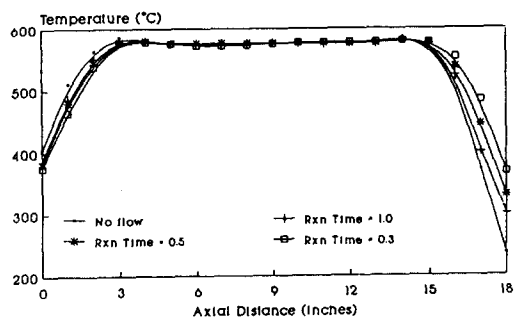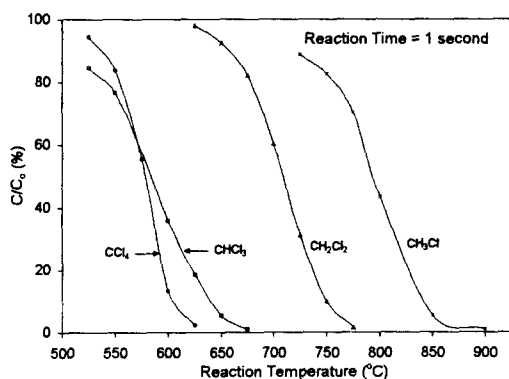Fig. 2. Reactor temperature profiles with tight control.

Fig. 3. Comparison of thermal stability for choromethanes.

sation.

The quartz tube reactor of 8 mm ID was hosed within a three zone electric tube furnace 32 inches in length equipped with three independent temperature controllers. The actual temperature profile of the tubular reactor was obtained using a type K thermocouple probe moving coaxially within reactor under steady state flow. The temperature profiles shown with varied flow rates in Figure 2 resulted from carefully adjusting the heat flux to the reactor at each different flow rate. Tight temperature control resulted in temperature profiles isothermal within $\pm 3°C$ over 75% of the furnace length for all temperature ranges of this study.

2.2 Analytical Methods

A HP 5890 on-line gas chromatograph with FID was used to determine concentrations of the reaction products. The GC used a 5 ft long by 1.8 inch o.d. stainless steel column packed with 1% Alltech

AT-1000 on graphpac GB as the column. A six port gas sample valve with a 0.5 ml volume loop was used to inject sample and was maintained at 170°C and 1 atm pressure.

Quantitative analysis of HCl was performed for each run. The samples for HCl analysis were collected independent from GC sampling. Reactor effluent was diverted through to bubbler trains containing 0.01 M NaOH before being exhausted to a fume hood. The HCl produced was then calculated based on titration of the bubbler solution with 0.01 M HCl to its phenolphthalein end point.

3. RESULTS AND DISCUSSION

3.1 Decay of Pure Compound Methanes

Figure 3 depicts thermal degradation profiles of chloromethanes for each pure compound as function of temperatures at 1 second reaction time under excess hydrogen atmosphere. The parent thermal stability (defined by the temperature required for 99% destruction) was evaluated as 875°C for CH_3Cl, 780°C for CH_2Cl_2, 675°C for $CHCl_3$ and 635°C for CCl_4. The Least Bond Dissociation Energy (LBDE) of chloromethanes is 83.6 Kcal/mol for CH_3Cl, 80.8 Kcal/mol for CH_2Cl_2, 76.6 Kcal/mol for $CHCl_3$ and 68.8 Kcal/mol for CCl_4 (Weissman and Benson, 1983). The 99% destructions of each pure chloromethanes were in agreement with LBDE trend. This implies the less chlorinated methanes are more stable. It is consistent with the bond strengths of C-Cl bonds on C1 chlorocarbons which increase with decreasing chlorination.

However, close inspection of Figure 3 indicates that $CHCl_3$ was initially less stable than CCl_4. The reason is that a low activation energy of three center HCl elimination reaction is responsible for the rapid decomposition of $CHCl_3$ at fairly low temperatures ($<570°C$), although LBDE of $CHCl_3$ is larger than that of CCl_4.

Transition State Theory (Benson, 1976) for a simple bond cleavage (1b), estimates a loose configuration and Arrhenius A factor that is higher

than the three center HCl elimination (1a) which has a tight transition state. However, the barrier height for HCl molecular elimination is sometimes significantly lower than the simple bond cleavage. There are previous studies (Kung and Bissinger, 1964; Benson and Spokes, 1966; Schug et al., 1979; Herman, et al., 1983; Won and Bozzaelli, 1992) which suggested that reaction (1a) dominates reaction (1b). We also feel strongly that : $CCl_2 + HCl$ is the dominant initiation decomposition path for $CHCl_3$ in experimental results based upon product distributions (Won and Bozzelli, 1992).

$$CHCl_3 \rightarrow\, : CCl_2 + HCl \tag{1a}$$
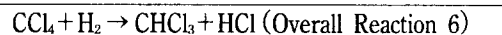$$CHCl_3 \rightarrow CHCl_2 + Cl \tag{1b}$$

The decomposition of CCl_4 became more sensitive to increasing temperature, and the decay curve of $CHCl_3$ crossed at 570°C (40% destruction) with CCl_4 more easily degraded above 570°C as illustrated in Figure 3.

The acceleration of CCl_4 decomposition with increasing temperature resulted from several combinated effects:

1. The C-Cl bond dissociation energy (68.8 Kcal/mol) of CCl_4 is lower than that (76.6 Kcal/mol) of $CHCl_3$, leading to much more sufficient Cl atom formed from CCl_4 than $CHCl_3$.

2. The Cl atom has high Arrhenius A factor and low activation energy for abstraction of H from H_2 (reaction (3)).

3. The H atom generated rapidly undergoes abstraction reaction (4) which rapidly regenerate H atom (reaction (5)) and continue the chain reactions.

4. The Cl atom generated from reaction (2) is more reactive than CCl_2 generated from reaction (1a): Therefore, chain reactions was easily occurred in reaction system of CCl_4 than in that of $CHCl_3$.

5. Particularly, in the chloroform reaction system, dichlorocarbene from dominant initiation reaction of chloroform reacted with hydrogen bath gas to form the stable methylene chlo-

ride through the termination of chain reaction as shown in reaction (7).

$$CCl_4 \rightarrow CCl_3 + Cl \tag{2}$$
$$Cl + H_2 \rightarrow H + HCl \tag{3}$$

$$CCl_4 + H \rightarrow CCl_3 + HCl \tag{4}$$
$$\underline{CCl_3 + H_2 \rightarrow CHCl_3 + H} \tag{5}$$
$$CCl_4 + H_2 \rightarrow CHCl_3 + HCl \text{ (Overall Reaction 6)}$$
$$CCl_2 + H_2 \rightarrow CH_2Cl_2 \tag{7}$$

As a result of thermochemical consideration, one may expect sufficient Cl atom concentration in CCl_4 pyrolysis reaction system, because CCl_4 has the lowest C-Cl bond energy of chloromethanes. The acceleration of CCl_4 decay results from the abstraction (4) by H of Cl from CCl_4, and from reaction (2). H is produced from reaction of Cl with the H_2 bath gas as reaction (3). The Cl atom from initiation reaction of CCl_4 (reaction (2)) reacts with the hydrogen bath gas to form H atom and HCl as reaction (3).

The H atom accelerates decomposition of CCl_4 by Cl abstraction reaction (4). In reaction (4), H atom is consumed, but H atom is produced in reaction (5). So, H atom is not consumed apparently as listed in overall reaction (6). The H atom cyclic chain reaction plays a catalytic role in the acceleration of CCl_4 decomposition.

3.2 Product Distribution in CCl_4/H_2 Reaction System

Figure 4 presents the reactant and product distributions identified by GC analyses in a hydrogen excess environment as a function of temperature at 1 second reaction time. Complete destruction (99%) of the parent reagent was observed at temperature near 635°C with residence time over 1 second. The major products observed were $CHCl_3$, CH_2Cl_2, C_2Cl_4 and HCl below 635°C where up to complete conversion (99%) of CCl_4.

The formation of chloroform increases proportional to decrease in carbon tetrachloride at below 635°C. The formation of chloroform formation was
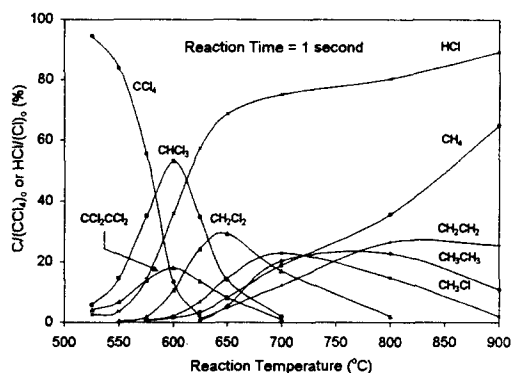
Fig. 4. Product distribution vs temperature in CCl₄/H₂.

occurred due to Cl simple dissociation of CCl_4 to form CCl_3 radical and Cl atom. CCl_3 radicals react with hydrogen bath gas to produce primary product, $CHCl_3$ as listed in reaction (5). The other formation pathway of chloroform is Cl abstraction by H atom as described in acceleration of CCl_4 destruction (reaction (4) − (6)).

The decomposition for chloroform drops quickly as temperature increases up to 700℃, where methylene chloride increases. This implied that methylene is the secondary product. Formation of CH_2Cl_2 increases with increasing temperature to a maxima near 650℃ and then drop slowly. Formation of methyl chloride also shows the same trend but with maxima around 700℃. The only methyl chloride was observed at above 800℃ with HCl and CH_4 formation increasing. The methane is then produced from further reaction of methyl chloride with hydrogen gas.

Maximum concentrations of chloromethane as intermediate products are found as 600℃ for chloroform, 650℃ for methylene chloride and 700℃ for methyl chloride. From Figure 4, it is clearly demonstrated that one less chlorinated methane than parent increase with temperature rise subsequently. The number and quantity of chlorinated products decreases with increasing temperature. Formation of non-chlorinated hydrocarbons increased as the temperature increased and particularly small amount of methyl chloride was observed above 850
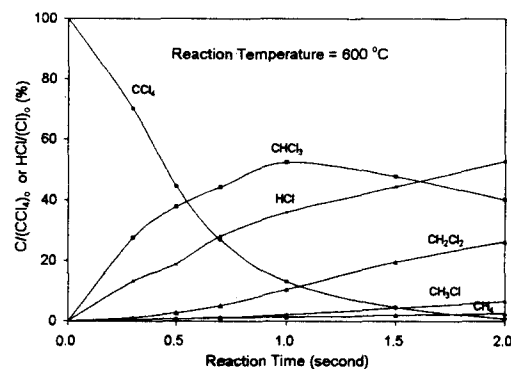

Fig. 5. Product distribution vs time in CCl₄/H₂.

Table 1. Material Balance for 100 Moles Carbon at 1 Second Reaction Time (CCl₄ : H₂=4 : 96)

Species (mole (%))	Reaction Temperature (℃)							
	525	575	600	625	650	700	800	900
CH₄	ND	0.6	1.5	3.3	8.1	18.8	35.5	65.1
CHCH	ND	ND	0.2	0.9	1.8	2.7	2.1	1.2
CH₂CH₂	ND	ND	ND	1.1	4.8	12.3	26.4	25.5
CH₃CH₃	ND	ND	ND	0.8	5.3	20.4	22.7	10.8
CH₃Cl	ND	0.6	2.2	7.0	14.4	22.9	14.7	0.5
CHCCl	ND	ND	0.1	0.3	0.7	0.6	ND	ND
CH₂CHCl	ND	ND	0.3	2.5	4.8	3.2	ND	ND
CH₃CH₂Cl	ND	ND	ND	1.3	3.1	0.6	ND	ND
CH₂Cl₂	ND	1.7	10.6	24.4	29.3	17.0	1.0	ND
CClCCl	ND	ND	ND	ND	0.2	ND	ND	ND
C₄H₁₀	ND	ND	ND	ND	0.1	ND	ND	ND
CH₂CCl₂	ND	0.1	1.4	3.4	3.1	1.4	ND	ND
CH₃CHCl₂	ND	ND	0.4	1.8	1.1	ND	ND	ND
CHCl₃	5.7	34.9	53.1	34.8	14.1	0.5	ND	ND
CCl₄	ND	94.5	55.5	13.2	2.1	ND	ND	ND
CHClCCl₂	ND	0.7	5.0	7.1	4.7	1.2	ND	ND
C₆H₆	ND	ND	ND	0.2	0.7	1.6	2.1	2.3
CCl₂CCl₂	4.2	13.8	17.9	13.6	8.2	2.5	ND	ND
C₆H₅CH₃	ND	ND	ND	ND	0.2	0.2	0.3	ND
C₆H₅Cl	ND	ND	ND	0.2	0.6	0.9	0.5	ND

(ND : less than 0.1 carbon mole (%))

℃. This indicates the less chlorinated products are more stable, with methyl chloride the most stable chlorocarbon in this reaction system.

Figure 5 shows the product distribution from

the pyrolysis of carbon tetrachloride as function of reaction time at 600℃ reaction temperature under excess hydrogen atmosphere. Also, The formation of chloroform increases as reaction time rises upto 1.0 second, where carbon tetrachloride drops quickly. With reaction time rise again, the chloroform decreases to be a maxima around 1.0 second and the formations of methylene chloride and methyl chloride increase. Product distribution against reaction time as shown in Figure 4 demonstrates similar trend to that against reaction temperature as shown in Figure 3. Table 1 listed the carbon material balance for product concentrations of carbon tetrachloride reaction system with temperature including minor products. The various chloroethylenes were detected over wide reaction temperature as listed in table 1. The highly chlorinated ethylenes such as perchloroethylene and trichloroethylene are observed at lower reaction temperature range. The less chlorinated ethylenes increases with increasing temperature as like dechlorination process of chloromethanes. Chloroethylenes are formed as a consequence of chloromethyl and CCl_2 radicals which undergo combination and insertion process via the initial formation of chemical activated adducts.

Perchloroethylene was only major ethylene compound product ($<5\%$) at low reaction temperature ranges. Dichlorocarbene is key species to form perchloroethylene. As listed in reaction (8), the formation of dichlorocarbene resulted from unusual dissociation of CCl_3 formed from reaction (2) and (4). Michael et al. (1993) reported that two Cl atoms are ultimately produced for each CCl_4 that dissociates, with the secondary Cl atom forming slower than the first, as the secondary Cl atom fission (reaction (8)) at a rate about 0.1 that of primary fission (reaction (2)).

$$CCl_3 \rightarrow CCl_2 + Cl \tag{8}$$

Formation of perchloroethylene results from combination of two CCl_2 radicals as reaction (9).

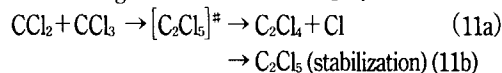$$CCl_2 + CCl_2 \rightarrow [C_2Cl_4]^{\#} \rightarrow C_2Cl_4 \tag{9}$$
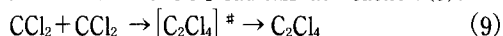
Another formation pathway for perchloroethylene is the insertion of CCl_2 into chloroform as primary

product in carbon tetrachloride reaction system. The activated complex of pentachloroethane is formed at the energy of the reactants. It can be stabilized or react to $C_2Cl_4 + HCl$ through HCl molecular elimination as low energy barrier exit channel. Also, the stabilized pentachloroethane is dissociated to form $C_2Cl_4 + HCl$.

$$CCl_2 + CHCl_3 \rightarrow [C_2HCl_5]^{\#} \rightarrow C_2Cl_4 + HCl \tag{10a}$$
$$\rightarrow C_2HCl_5(stabilization) \tag{10b}$$
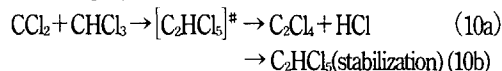
The dichlorocarbene react with CCl_3 results in chain propagation products to $C_2Cl_4 + Cl$, and C_2Cl_5 which undergo beta scission to $C_2Cl_4 + Cl$.

$$CCl_2 + CCl_3 \rightarrow [C_2Cl_5]^{\#} \rightarrow C_2Cl_4 + Cl \tag{11a}$$
$$\rightarrow C_2Cl_5 (stabilization) \tag{11b}$$

These highly chlorinated ethylenes convert to less chlorinated ethylene by H atom addition reaction and H atom cyclic chain reactions.

Chloroethylenes are dechlorinated by H addition displacement reactions which are important channels for reducing the chlorine content of unsaturated chlorocarbons. Atomic H can add to C_2Cl_4 to form C_2HCl_4 radical as shown in reaction (12). The $[C_2HCl_4]^{\#}$ complex is initially "hot" since, in addition to the thermal energy, it contains energy resulting from the formation of the stronger C-H bond relative to Pi bond broken. Prior to stabilization, it may dissociate back to reactants, become a stabilized radical or beta scission to $C_2HCl_3 + Cl$.

$$C_2Cl_4 + H \rightarrow [C_2HCl_4]^{\#} \rightarrow C_2HCl_3 + Cl \tag{12}$$
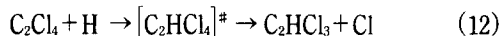
Another reaction pathways to form C_2HCl_3 from C_2Cl_4 are the unimolecular decomposition and Cl abstraction by H atom. C_2Cl_4 is decomposed by unimolecular decomposition to form $C_2Cl_3 + Cl$ as reaction (13). The H atom from reaction (3) abstracts Cl resulting in $C_2Cl_3 + HCl$ as like acceleration pathway of CCl_4 decomposition. And C_2Cl_3 radicals formed from reaction (13) and (14) reacts with excess hydrogen to form C_2HCl_3 as follow:

$$C_2Cl_4 \rightarrow C_2Cl_3 + Cl \tag{13}$$
$$C_2Cl_4 + H \rightarrow C_2Cl_3 + HCl \tag{14}$$
$$C_2Cl_3 + H_2 \rightarrow C_2HCl_3 + H \tag{15}$$

Dichloroethylene is produced from further reaction of trichloroethylene via H addition reaction

E (Kcal/mol)
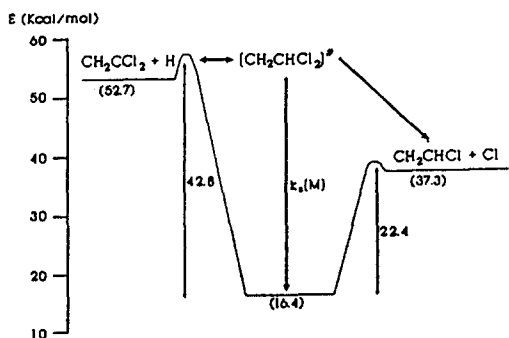
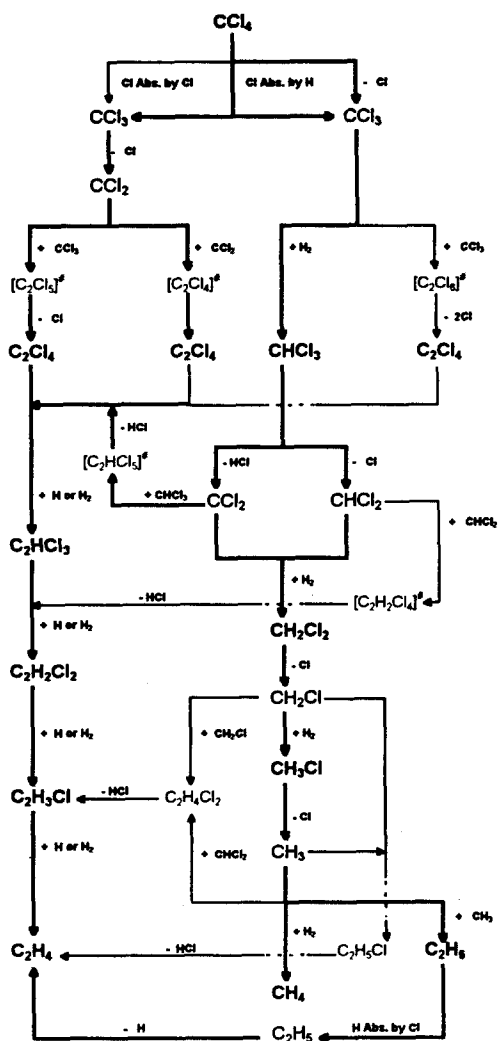
Fig. 6. **Potential energy diagram for CH₂CCl₂+ H addition reaction.**

Fig. 7. **Detailed Reaction Pathways in CCl₄/H₂.**

and H atom cyclic chain reaction.

In Figure 6, energy diagram shows for $H + CH_2$ CCl_2 addition reaction to form vinyl chloride. The H atom addition reaction is important for reducing the chlorine contents of unsaturated chlorocarbons including aromatics. This H addition reaction results in formation of vinyl chloride and Cl atom through Cl kick out reaction. Vinyl chloride is decomposed similar to decomposition of dichloroethylene. Finally, ethylene as hydrodechlorinated product was formed in elevated temperature range.

Figure 7 summarized the main reaction pathway to form hydrodechlorinated products from carbon tetrachloride. This overall reaction scheme based on analysis of the observed products and thermochemical kinetics estimation was illustrated in Figure 7.

4. CONCLUSIONS

The reaction of excess hydrogen with pure compound chloromethanes; methyl chloride, methylene chloride, chloroform and carbon tetrachloride has been studies in an isothermal tubular flow reactor at a pressure of 1 atm and in the temperature range 525~900℃.

The parent thermal stability on basis of temperature required for 99% destruction at 1 second reaction time was evaluated as 875℃ for CH_3Cl, 780℃ for CH_2Cl_2, 675℃ for $CHCl_3$ and 635℃ for CCl_4. Chloroform was thermally less stable than CCl_4 at fairly low temperatures (<570℃) due to the low activation energy of three center HCl elimination reaction of chloroform. The decomposition of CCl_4 became more sensitive to increasing temperature and CCl_4 was degraded easier than $CHCl_3$ above 570℃. The reason was that H atom cyclic chain reaction played a catalytic role in decomposition of CCl_4.

The number and quantity of chlorinated products decreases with increasing temperature for the product distribution of CCl_4 decomposition reaction system. Maximum concentrations of chloromethane as intermediate products were observed as 600℃ for chloroform, 650℃ for methylene chloride and 700

℃ for methyl chloride in CCl_4/H_2 reaction system. It is demonstrated that one less chlorinated methane than parent increase with temperature rise subsequently. Formation of non-chlorinated hydrocarbons such as methane, ethylene and ethane increased as temperature rise and particularly small amount of methyl chloride was found at above 850 ℃. The less chlorinated products are more stable, with methyl chloride the most stable chlorocarbon in this reaction system.

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과잉수소 반응조건하에서 사염화탄소의
고온 분해반응 특성 연구

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(1996년 8월 13일 접수)

과잉수소 반응조건하에서 사염화탄소의 열적 안정성과 수첨탈염소화 과정을 고찰하기 위한 모델로써 Cl/H의 비가 다른 순수 염화메탄화합물인 메틸염소, 메틸렌염소, 클로로포름과 사염화탄소를 이용하였다. 반응시간 1초에서 99% 분해되는 온도를 기준으로한 열적 안정성은 메틸염소는 875℃, 메틸렌염소는 780℃, 클로로포름은 675℃, 사염화탄소는 635℃ 이었으며, 낮은 반응온도영역에서는 클로로포름의 열적 안정성이 사염화탄소보다 낮았으나 온도가 증가함에 따라 사염화탄소의 분해가 증가하여 570℃ 이상에서는 클로로포름보다 쉽게 분해되었다.

사염화탄소의 분해 반응계에서의 생성물 고찰결과, 반응온도가 증가함에 따라 염화탄화수소 화합물 계열 생성물의 농도와 염화정도가 감소하였다. 과잉수소 반응조건에서 사염화탄소 열분해 실험결과, 850℃ 이상에서는 탈염소화 탄화수소화합물인 메탄, 에틸렌, 에탄의 생성물의 농도가 증가하였으며 염소화 합물로는 메틸염소만이 소량 검출되었다. 이는 염화정도가 낮은 화합물일수록 열적 안정성이 크다는 것을 의미하며 CCl$_4$/H$_2$ 반응계에서 염화탄소화합물중 메틸염소가 열적 안정성이 가장 큰 화합물이었다.