Comparison for thermal decomposition and product distribution of chloroform under each argon and hydrogen reaction atmosphere

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(*Received 6 March 2012 • accepted 4 June 2012*)

Abstract−Thermal reaction studies of diluted mixture (1%) of chloroform ($CHCl_3$) under each argon (Ar) and hydrogen (H_2) reaction atmosphere have been investigated to examine the effect of reaction atmosphere on decomposition of $CHCl_3$ and product distributions. The experimental results were obtained over the temperature range 525-900 °C with reaction times of 0.3-2.0 sec. at 1 atm by utilizing an isothermal tubular flow reactor. Complete destruction (>99%) of the parent reagent, $CHCl_3$ was observed near 675 °C under H_2 reaction atmosphere ($CHCl_3/H_2$ reaction system) and 700 °C under Ar reaction atmosphere ($CHCl_3/Ar$ reaction system) with 1 sec reaction time. The $CHCl_3$ pyrolysis yielded more conversion in H_2 atmosphere than in Ar atmosphere. Major products in $CHCl_3/Ar$ reaction system were C_2Cl_4, CCl_4, C_2HCl_3 and HCl over a wide temperature range. Hydrocarbon was not found in $CHCl_3/Ar$ reaction system. Major products of $CHCl_3/H_2$ reaction system observed were CH_2Cl_2, CH_3Cl, CH_4, C_2Cl_4, C_2HCl_3, $C_2H_2Cl_2$, C_2H_3Cl and HCl at 600 °C with 1 sec. reaction time. Non-chlorinated hydrocarbons such as CH_4, C_2H_4 and C_2H_6 were the major products at above 850 °C. Product distributions were distinctly different in Ar and H_2 reaction atmospheres. The H_2 gas plays a key role in acceleration of reagent decay and formation of non-chlorinated light hydrocarbons through hydrodechlorination process. The important reaction pathways, based on thermochemical and kinetic principles, to describe the features of reagent decay and intermediate formation under each Ar and H_2 reducing reaction atmosphere were investigated.

Key words: Thermal Decomposition, Chloroform, Hydrogen, Argon, Reaction Pathway

INTRODUCTION

The incineration of hazardous wastes presents effective disposal methodology; nevertheless, the use of this technology has been severely hindered by environmental concerns regarding the effluents from such system [1]. Two important issues are the capability of incinerators to effect the high level of destruction that is desired, and the possibility that other hazardous chemicals may be formed and thus impact the environment [2]. The overall incineration process is complex and involves interactions of chemistry, heat transfer, and fluid dynamic phenomena. Louw et al. [3], for example, note that operating conditions of 1,000 K and several minutes are needed to limit incinerators with certain hazardous feeds from emitting intolerable amounts of polychlorinated dibenzodioxins (PCDD).

Chlorinated hydrocarbons (CHCs) are generally incinerated in an oxygen-rich environment. It 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. In considering products from incineration, the bond of H-Cl is the strongest and has the lowest Gibbs free energy of formation per chlorine atom. The HCl is, therefore, the thermodynamically favored product for chlorine, providing there exists sufficient hydrogen for its stoichiometric formation [4]. However, the O-H bond in H_2O is stronger than the H-Cl bond, and the O_2 rich conditions limit hydrogen availability. The C-Cl bond is the next strongest compared with other possible chlorinated products such as Cl-Cl, N-Cl, or O-Cl bonds

[5,6]. Consequently, the C-Cl bond may persist in a hydrogen-lean and oxygen-rich atmosphere. This suggests that the emission of toxic chlorine containing organic products may persist through an oxygen-rich incineration, as it is one of the more stable sinks for the chlorine.

To obtain a quantitative formation of HCl, as one of the desired and thermochemically favorable products, from chlorinated hydrocarbons, one might use a straightforward thermal conversion of these compounds under a more reductive atmosphere of hydrogen. The non-oxygen methods were developed in order to avoid the formation of undesired oxy-containing products, such as phosgene and dioxins [7,8]. The chlorocarbon and hydrogen system contains only C, H, and Cl elements and is expected to lead to the formation of light hydrocarbons and hydrogen chloride at the temperatures where complete reaction occurs. Under such a system, carbon can be converted to CH_4, C_2H_2, C_2H_4 and C_2H_6 [9,10].

The objectives of this work are

• Examine thermal reaction of chloroform to investigate product distributions and main reaction pathways to form various products under each non-reactive (Ar) and reactive (H_2) gas reaction environment.

• Investigate synergistic effects of chloroform decomposition and hydrodechlorination process in H_2 reductive reaction environment.

• Determine if complete and facile conversion to desired and thermodynamically favorable products, hydrocarbons and HCl easily scrubbed is achievable in H_2 reaction atmosphere.

• Characterize product distributions and the effect of H_2 on pyrolysis processes comparing with $CHCl_3/Ar$ reaction system.

• Formulate major reaction pathways based on thermochemical & kinetic principles and experimental results with different reduc-

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ing reaction atmospheres.

• Enhance understanding of thermal reaction kinetics of C/H/Cl system.

These reaction systems are not realistic incineration processes. Pyrolysis is important to understand in addition to oxidation, because it occurs in two regions of an incinerator: i) in the feed process where mixing is not complete, and ii) in the effluent stream where O_2 is depleted (atmosphere of CO_2 and H_2O) when poor mixing allows organics to make it through the incinerator process. This study characterized the reactant loss and intermediate product formation to describe the reaction process under each Ar and H_2 reaction atmosphere.

EXPERIMENTAL METHOD

Chloroform ($CHCl_3$) was reacted under each Ar and H_2 reaction atmosphere in an isothermal tubular reactor at 1 atm. The products of such thermal degradation were analyzed by varying the temperature from 525 to 900 °C and the residence time from 0.3 to 2.0 sec. A diagram of the experimental system is shown in Fig. 1. The gas (Ar or H_2) was passed through a multi-saturator train held at 0 °C to ensure saturation with $CHCl_3$ at a constant reference temperature for accurate vapor pressure calculation. A second (dilutent) stream of atmosphere gas (Ar or H_2) was used to achieve the desired mole fraction of 1% $CHCl_3$ that was maintained through the whole experiment. The reagent ($CHCl_3$) with Ar or H_2 gas was fed continuously into an isothermal tubular flow reactor in the vapor phase. The quartz tube reactor of 8 mm ID was hosed within a three zone electric tube furnace of 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. Tight temperature control resulted in temperature profiles isothermal within ±3 °C over 80% of the furnace length for all temperature ranges of this study.

An HP 5890IIon-line GC with FID was used to determine concentrations of the reaction products. The GC used a 5 ft long column packed with 1% Alltech AT-1000 on graphpac GB as the column. A six port gas sample valve was used to inject sample. Quantitative analysis of HCl was performed for each run. 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. The experimental apparatus and procedures used this study are similar to those used in our earlier studies [4,11]. Therefore, only a brief summary of these subjects is given.

RESULTS AND DISCUSSION

1. Comparison for Decomposition of $CHCl_3$ in Each Reaction Atmosphere

Transition state theory predictions for a simple bond cleavage of $CHCl_3$, such as reactions (1b) and (1c), will typically show a loose configuration [12]. The Arrhenius A factors of reactions (1b) and (1c) will be higher than that of the three center HCl elimination reaction (1a) which has a tight transition state [13]. However, the barrier height for HCl molecular elimination is sometimes significantly lower than the simple bond cleavage. The reaction rate constant for reaction (1a) at 600 °C based on calculation of listed kinetic parameters is by 300 times larger than for reaction (1b). Also, there are previous studies [14-17] 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 $CHCl_3$ decay and product distributions.

Fig. 2 compares $CHCl_3$ decay as function of temperatures at 1 sec reaction time under each Ar and H_2 reaction environment. Complete destruction (>99%) of the parent reagent, $CHCl_3$ was observed near 675 °C in H_2 atmosphere ($CHCl_3/H_2$ reaction system) and 700 °C
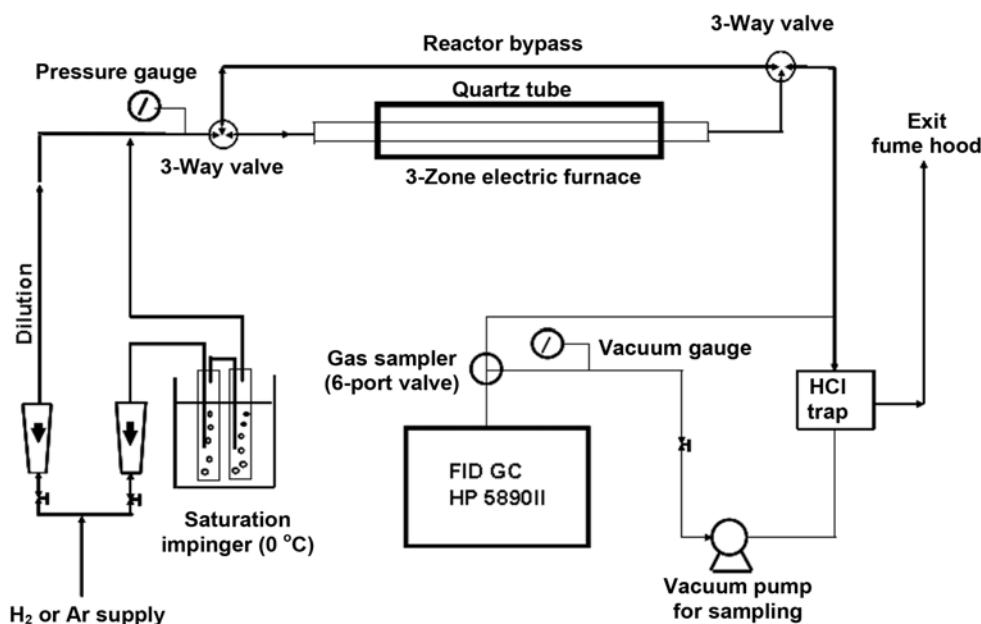

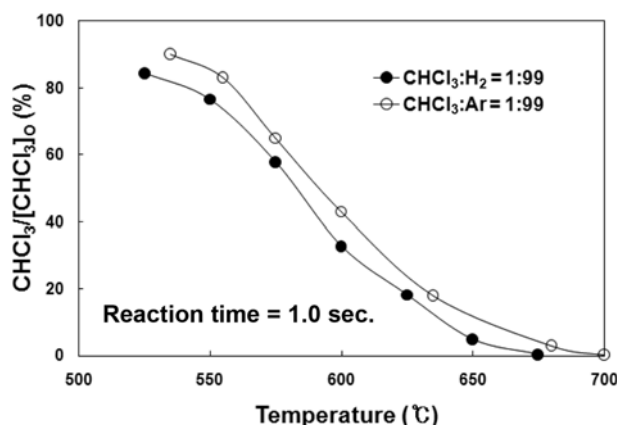Fig. 1. Schematic diagram of experimental system.

Table 1. Kinetic parameters for unimolecular decomposition of CHCl₃

Reaction	Reaction rate parameter			Ref.	rxn no.
	A^a	Ea^b	$k_{(600\ ^oC)}{}^c$		
$CHCl_3 \rightarrow :CCl_2 + HCl$	1.6E14	56.0	1.53	[12,13]	(1a)
$CHCl_3 \rightarrow CHCl_2 + Cl$	2.5E16	74.6	5.3×10^{-3}	[13,18]	(1b)
$CHCl_3 \rightarrow CCl_3 + H$	1.7E16	96.0	1.6×10^{-8}	[13,18]	(1c)

Kinetic parameters estimated from similar reaction in [12], [13] & [18]

[a]A factors based on entropy change for reverse reaction in [12] & [18]
 A unit: (1/s) for unimolecular reaction, (cm^3/mols) for bimolecular reaction

[b]Ea unit: kcal/mol, [c]k unit: mol/cm^3s

Fig. 2. Comparison of CHCl₃ decay in CHCl₃/H₂ and CHCl₃/Ar reaction system.

Fig. 3. Product distribution vs. temperature in CHCl₃/Ar reaction system.

Fig. 4. Product distribution vs. reaction time in CHCl₃/Ar reaction system.

in inert Ar atmosphere (CHCl₃/Ar reaction system) with 1 sec reaction time. The faster CHCl₃ decay occurs in H₂ reaction atmosphere. The H₂ atmosphere has an effect on accelerated decomposition of CHCl₃. The H₂ reaction atmosphere served to accelerate the decomposition of CHCl₃ by a series chain reactions resulting from H atom which was produced from reaction of radical and atom with H₂. The detailed discussions for acceleration of CHCl₃ decay under H₂ atmosphere will be made in part of reaction pathway for CHCl₃/H₂ system.

2. Product Distributions for CHCl₃/Ar Reaction System

Fig. 3 presents the parent reactant decay and product distributions identified by GC analysis in Ar reaction atmosphere. Carbon mole fraction of products relative to initial number of carbon mole of CHCl₃ injected (C/C_o) is plotted versus reaction temperature at 1 sec reaction time. Complete destruction (99%) of the CHCl₃ was observed near 700 °C with residence time 1 sec. The formation of C₂Cl₄ and HCl increases proportionally to the decrease in CHCl₃. Major products were C₂Cl₄ and HCl over a wide temperature range, and small amounts of CCl₄ and C₂HCl₃ were observed. Most of products were perchlorocarbons under inert gas Ar reaction atmosphere. No hydrocarbon was found in CHCl₃/Ar reaction system. The Ar atmosphere reaction system gave simple product distributions as compared with the H₂ atmosphere reaction system (see Fig. 5) because the reaction atmosphere gas is inert.
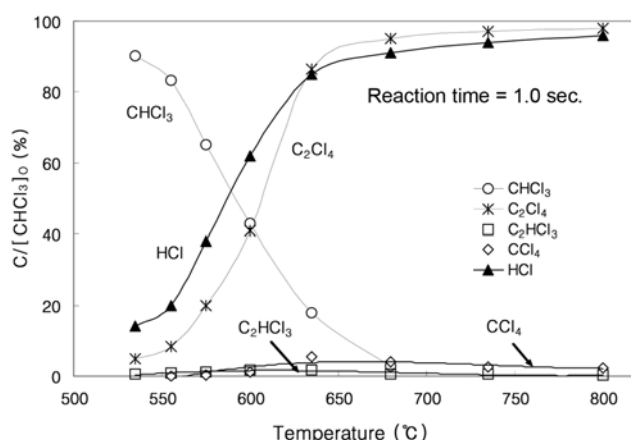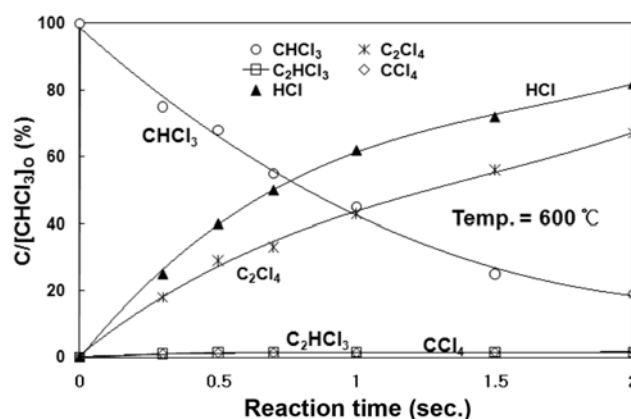
Fig. 4 shows the product distribution in pyrolysis of CHCl₃ as function of reaction time at 600 °C under Ar reaction atmosphere. The formations of C₂Cl₄ and HCl increase with a reaction time, where CHCl₃ drops quickly. Tiny amounts of CCl₄ and C₂HCl₃ were observed. The product profiles against reaction time as shown in Fig. 4 demonstrate a similar trend to those against reaction temperature as shown in Fig. 3.

3. Product Distributions for CHCl₃/H₂ Reaction System

Fig. 5 presents the reactant(CHCl₃) and product distributions in H₂ reaction environment as a function of temperature at 1 sec reaction time. The complete decay (99%) of CHCl₃ was observed near 675 °C with reaction time 1 sec. The major products observed were CH₂Cl₂, CH₃Cl, C₂Cl₄, CH₄, C₂H₄, C₂H₆ and HCl below 675 °C where up to complete conversion (99%) of CHCl₃. Trace amounts of C₂HCl₃, CH₂CCl₂, C₂H₃Cl, C₂H₅Cl, C₂H₄Cl₂ and C₂H₂ (not presented in Fig. 5) were detected. Non-chlorinated hydrocarbons, such as CH₄, C₂H₄ and C₂H₆ were detected over reaction temperature 850 °C. The H₂ reaction atmosphere led to the formation of various products as compared with Ar reaction atmosphere (see Fig. 3) because of the presence of reactive gas.

Maximum concentrations of chloromethane as intermediate products are found as 625 °C for CH₂Cl₂ and 750 °C for CH₃Cl. Formation of CH₂Cl₂ increases with increasing temperature to a maximum
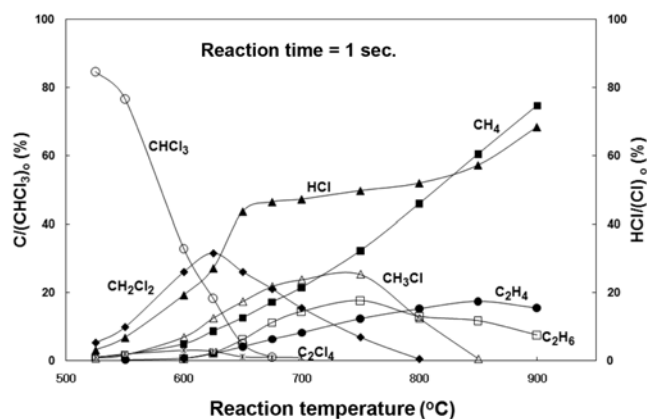
Fig. 5. Product distribution vs. temperature in CHCl₃/H₂ reaction system.

near 625 °C and then drops slowly. Formation of CH₃Cl also shows the same trend but with maxima around 700 °C. The formation of CH₃Cl increases proportional to decrease in CH₂Cl₂ at below 750 °C. The CH₄ is finally produced from further reaction of CH₃Cl with H₂ atmosphere gas.

From Fig. 5, it is demonstrated that one less chlorinated methane than parent compound increases with temperature rise subsequently. The chloromethane reacts with H₂ bath gas and to produce chloromethane with one less Cl than the parent. The number and quantity of chlorinated products decreases with increasing temperature. Formation of non-chlorinated hydrocarbons such as CH₄, C₂H₄ and C₂H₆ increased as the temperature increased. This indicates the less chlorinated products are more stable, with CH₃Cl the most stable chlorocarbon in this reaction system.

Fig. 6 shows the product distribution from thermal decomposition of CHCl₃ as function of reaction time at 625 °C under H₂ reaction atmosphere. Also, the formation of products increases as reaction time rises up to 1.0 sec, where reactant CHCl₃ drops quickly. With reaction time rise again, the products increase slowly and reach an apparent steady state. Product distribution against reaction time as shown in Fig. 6 demonstrates a similar trend to that against reaction temperature as shown in Fig. 5.

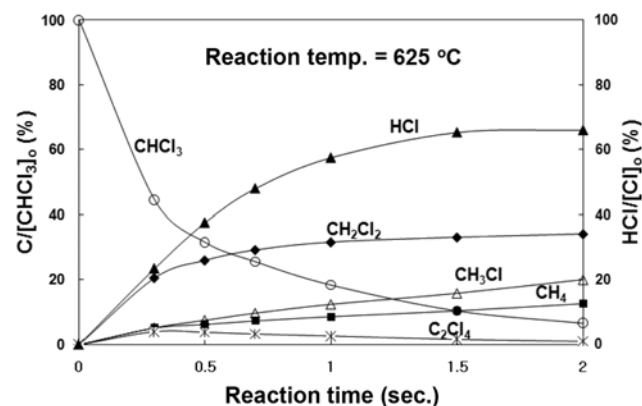Fig. 7 shows the formation of C₂Cl₄ as a function of reaction tem-

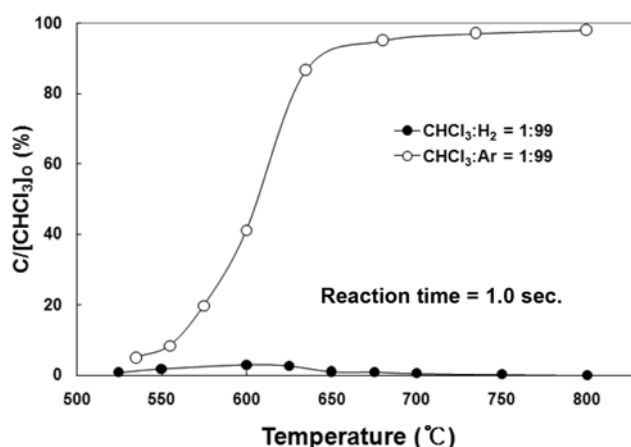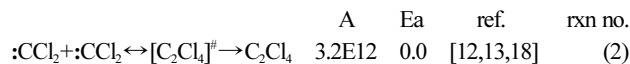**Fig. 6. Product distribution vs. reaction time in CHCl₃/H₂ reaction system.**

Fig. 7. Comparison of C₂Cl₄ formed per mole of CHCl₃ in Ar and H₂ reaction atmosphere.
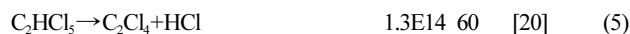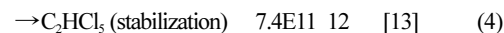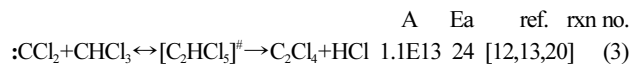
perature at 1 sec reaction time under each Ar and H₂ reaction environment. The CHCl₃/Ar reaction system produces a large amount of C₂Cl₄. Most of CHCl₃ is rearranged to form C₂Cl₄ under Ar reaction atmosphere because of the absence of reactive bath gas H₂. When the H₂ was present, the various products were formed instead of formation of C₂Cl₄. The detailed discussions for formation of C₂Cl₄ will be given in part of reaction pathway CHCl₃/Ar system.

4. Reaction Pathways for CHCl₃/Ar Reaction System

Perchloroethylene (C₂Cl₄) was a major product over wide reaction temperature ranges. The :CCl₂+HCl reaction (1a) pathway for unimolecular dissociation of CHCl₃ is favored over CHCl₂+Cl as discussed for the decay of CHCl₃. Dichlorocarbene (:CCl₂) is a key species to form perchloroethylene. C₂Cl₄ is formed by combination of two :CCl₂ radicals as reaction (2).

$$\text{:CCl}_2+\text{:CCl}_2 \leftrightarrow [\text{C}_2\text{Cl}_4]^\# \rightarrow \text{C}_2\text{Cl}_4 \quad\quad \begin{array}{cccc} A & Ea & ref. & rxn\ no. \\ 3.2E12 & 0.0 & [12,13,18] & (2) \end{array}$$

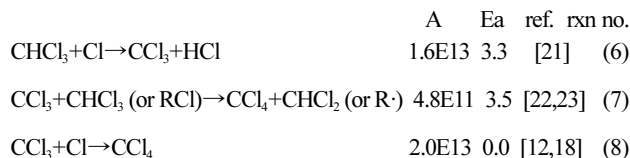Other pathways include :CCl₂ reactions with CHCl₃ (insertion) as reactant under Ar reaction atmosphere. The activated complex of $[\text{C}_2\text{HCl}_5]^\#$ is formed at the energy of the reactants. The energized complex $[\text{C}_2\text{HCl}_5]^\#$ can be stabilized or react to C₂Cl₄+HCl (chain termination). No stabilized C₂HCl₅ is detected because C₂HCl₅ is dissociated to form C₂Cl₄ through HCl molecular elimination reaction (5) as low energy barrier exit channel in this reaction condition [12,13,19].

$$\begin{array}{ccccc} & A & Ea & ref. & rxn\ no. \\ \text{:CCl}_2+\text{CHCl}_3 \leftrightarrow [\text{C}_2\text{HCl}_5]^\# \rightarrow \text{C}_2\text{Cl}_4+\text{HCl} & 1.1E13 & 24 & [12,13,20] & (3) \\ \rightarrow \text{C}_2\text{HCl}_5\ \text{(stabilization)} & 7.4E11 & 12 & [13] & (4) \\ \text{C}_2\text{HCl}_5 \rightarrow \text{C}_2\text{Cl}_4+\text{HCl} & 1.3E14 & 60 & [20] & (5) \end{array}$$

The product C₂Cl₄ is thermodynamically stable at this reaction condition. There is, in addition, limited hydrogen available to undergo reaction with this species. The chlorine abstraction by Cl atom is unlikely due to the large endothermicity. The C-Cl bond strength (88 kcal/mol) is higher than C-C bond strength (81.4 kcal/mol) [4, 12,13]. The C₂Cl₄ reaches an apparent steady state value, accounting for almost 100% of the parent CHCl₃ carbon between 680 and 800 °C.

The formation of CCl_4 as the only chlorine containing methane derivative product was observed. We attribute this to the reaction of Cl with parent $CHCl_3$, which forms the CCl_3 radical first by H atom a abstraction reaction (6). CCl_4 is then produced from reactions of CCl_3 with parent $CHCl_3$ and other chlorocarbon (C_2Cl_4 and so on) to form CCl_4+radical ($R\cdot$) and recombination with Cl atoms.

	A	Ea	ref.	rxn no.
$CHCl_3+Cl \rightarrow CCl_3+HCl$	1.6E13	3.3	[21]	(6)
CCl_3+CHCl_3 (or RCl)$\rightarrow CCl_4+CHCl_2$ (or R·)	4.8E11	3.5	[22,23]	(7)
$CCl_3+Cl \rightarrow CCl_4$	2.0E13	0.0	[12,18]	(8)

The minor product, C_2HCl_3, is formed from the combination of $CHCl_2$+$:CCl_2$ (9) and by combination of two $CHCl_2$ radicals (10). These two combination reactions are similar to formation pathways of C_2Cl_4 and proceed via initial formation of an activated complex.

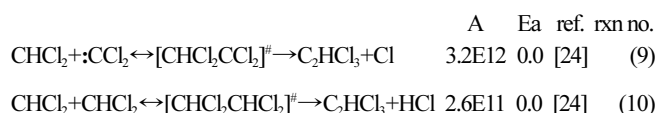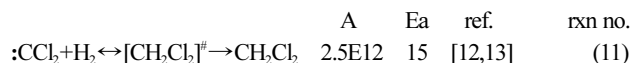|	A	Ea	ref.	rxn no.
$CHCl_2+:CCl_2 \leftrightarrow [CHCl_2CCl_2]^{\#} \rightarrow C_2HCl_3+Cl$	3.2E12	0.0	[24]	(9)
$CHCl_2+CHCl_2 \leftrightarrow [CHCl_2CHCl_2]^{\#} \rightarrow C_2HCl_3+HCl$	2.6E11	0.0	[24]	(10)

Fig. 8 summarizes the main reaction pathway for thermal decomposition of $CHCl_3$ with Ar reaction atmosphere. The important reaction scheme based on analysis of the observed products and thermochemical kinetics estimation is illustrated in Fig. 8.
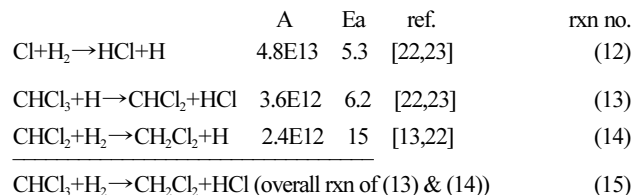
5. Reaction Pathways for $CHCl_3/H_2$ Reaction System

The CH_2Cl_2 is formed by insertion of $:CCl_2$, which results from reaction (1a), into atmosphere gas H_2 (11). The energy barrier for insertion process can be evaluated by noting the reverse barrier to $:CHCl+HCl$, which is determined by microscopic reversibility and thermodynamics [12]. The activated complex $[CH_2Cl_2]^{\#}$ can be stabilized to form CH_2Cl_2.

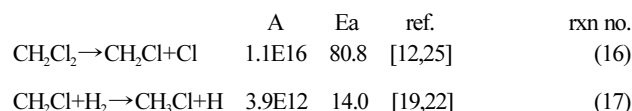|	A	Ea	ref.	rxn no.
$:CCl_2+H_2 \leftrightarrow [CH_2Cl_2]^{\#} \rightarrow CH_2Cl_2$	2.5E12	15	[12,13]	(11)

The other pathway for $CHCl_3$ decay results from the abstraction of Cl from $CHCl_3$ by H (13). The H atom can be produced from the reaction of Cl with H_2 bath gas as reaction (12). The Cl atom from initial decay of $CHCl_3$ (reaction (13)) reacts with H_2 to form
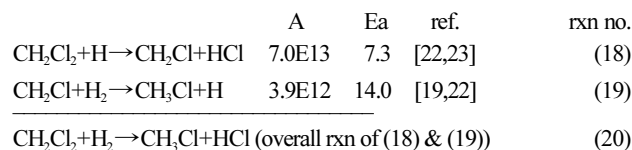
H and HCl by reaction (12). The H atom accelerates decomposition of $CHCl_3$ by Cl abstraction reaction (13). In reaction (13), the H atom is consumed, but the H atom is produced via reaction (14). So, the H atom is not consumed apparently as listed in overall reaction (15). The H cyclic chain reaction plays a catalytic role in the acceleration of $CHCl_3$ decomposition for $CHCl_3/H_2$ reaction system.

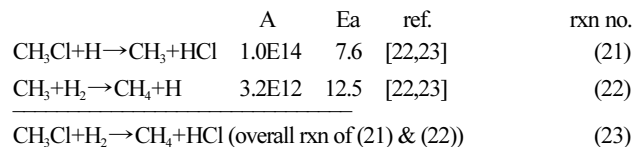|	A	Ea	ref.	rxn no.
$Cl+H_2 \rightarrow HCl+H$	4.8E13	5.3	[22,23]	(12)
$CHCl_3+H \rightarrow CHCl_2+HCl$	3.6E12	6.2	[22,23]	(13)
$CHCl_3+H_2 \rightarrow CH_2Cl_2+H$	2.4E12	15	[13,22]	(14)
$CHCl_3+H_2 \rightarrow CH_2Cl_2+HCl$ (overall rxn of (13) & (14))				(15)

The initiation of acceleration for decay of CH_2Cl_2 as primary product occurs due to Cl simple unimolecular dissociation of CH_2Cl_2 to form active species, CH_2Cl radicals and Cl atoms by reaction (16) at about 700 °C. The CH_2Cl radical reacts with H_2 bath gas to produce CH_3Cl as listed in reaction (17).

	A	Ea	ref.	rxn no.
$CH_2Cl_2 \rightarrow CH_2Cl+Cl$	1.1E16	80.8	[12,25]	(16)
$CH_2Cl+H_2 \rightarrow CH_3Cl+H$	3.9E12	14.0	[19,22]	(17)

The other decay pathway of CH_2Cl_2 is Cl abstraction by H atom (reaction (18)). The H atom reacts with CH_2Cl_2 and rapidly forms HCl and CH_2Cl radical. The CH_2Cl radical then reacts with H_2 to regenerate H atoms and to produce stable CH_3Cl with one less Cl than the parent compound. This process is exothermic and will continue on both the parent and product chlorocarbons until only hydrocarbons (and HCl) remain as described in acceleration of CH_2Cl_2 destruction (reaction (18) and (19)). The pathways for formation of CH_3Cl are similar to those for formation of CH_2Cl_2.

	A	Ea	ref.	rxn no.
$CH_2Cl_2+H \rightarrow CH_2Cl+HCl$	7.0E13	7.3	[22,23]	(18)
$CH_2Cl+H_2 \rightarrow CH_3Cl+H$	3.9E12	14.0	[19,22]	(19)
$CH_2Cl_2+H_2 \rightarrow CH_3Cl+HCl$ (overall rxn of (18) & (19))				(20)

CH_4 is also formed from further reaction of H abstraction cyclic chain reaction (21) and (22). The CH_3Cl decay as illustrated in reactions (21) is explained by a similar mechanism of CH_2Cl_2 loss. Finally, the CH_4 as non-chlorinated hydrocarbon is formed through reaction (22).

	A	Ea	ref.	rxn no.
$CH_3Cl+H \rightarrow CH_3+HCl$	1.0E14	7.6	[22,23]	(21)
$CH_3+H_2 \rightarrow CH_4+H$	3.2E12	12.5	[22,23]	(22)
$CH_3Cl+H_2 \rightarrow CH_4+HCl$ (overall rxn of (21) & (22))				(23)

CH_4 does not decrease with increasing reaction temperature at temperature of this work because of high activation energy (103.8 kcal/mol [12]) for unimolecular dissociation of CH_4. Some of CH_4 is decomposed by H abstraction reaction (24).

As shown in Fig. 4, some amount of C_2H_6 was observed over the wide reaction temperature. The C_2H_6 is formed as a consequence of two CH_3 radicals (resulting from reactions (21) & (24)) which undergo radical+radical combination reaction (25). The radical combination process has no energy barrier resulting in fast reaction.
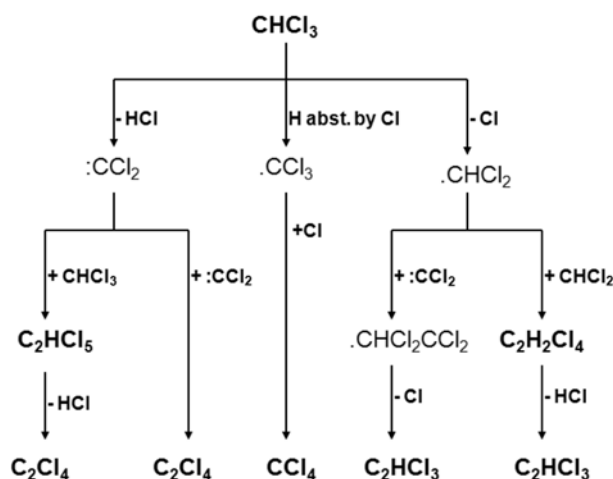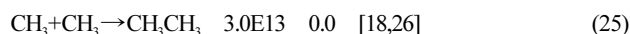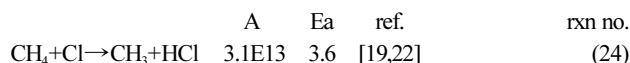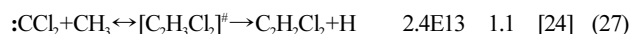

Fig. 8. Major reaction pathways for intermediate products in $CHCl_3/Ar$ reaction system.

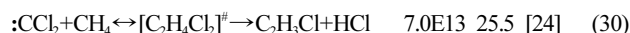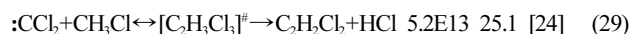|	A	Ea	ref.		rxn no.
$CH_4+Cl \rightarrow CH_3+HCl$	3.1E13	3.6	[19,22]		(24)
$CH_3+CH_3 \rightarrow CH_3CH_3$	3.0E13	0.0	[18,26]		(25)

The chloroethylenes are formed as a consequence of C_1 radicals ($:CCl_2$, $CHCl_2$, CH_2Cl & CH_3) and chloromethanes ($CHCl_3$, CH_2Cl_2, CH_3Cl & CH_4), which undergo combination and insertion processes via the formation of chemical activated adducts.

$C_2H_2Cl_2$ and C_2H_3Cl are formed from the combination of $:CCl_2$+ CH_2Cl (reaction (26)) and by combination of $:CCl_2+CH_3$ radicals (reaction (27)). The stabilized $[C_2H_2Cl_3]^{\#}$ and $[C_2H_3Cl_2]^{\#}$ radicals rapidly yield $C_2H_2Cl_2$ via beta scission.

		A	Ea	ref.	rxn no.
$:CCl_2+CH_2Cl \leftrightarrow [C_2H_2Cl_3]^{\#} \rightarrow C_2H_2Cl_2+Cl$		8.0E12	0.0	[13]	(26)
$:CCl_2+CH_3 \leftrightarrow [C_2H_3Cl_2]^{\#} \rightarrow C_2H_2Cl_2+H$		2.4E13	1.1	[24]	(27)

$:CCl_2$ reactions with chloromethanes (insertion) form the chloroethanes activated complexes ($[C_2H_2Cl_4]^{\#}$, $[C_2H_3Cl_3]^{\#}$ & $[C_2H_4Cl_2]^{\#}$). The stabilized chloroethanes will also dissociate to form chloroethylenes (C_2HCl_3, $C_2H_2Cl_2$ and C_2H_3Cl) and HCl through HCl molecular elimination reactions (28), (29) and (30) which have low energy barriers.

	A	Ea	ref.	rxn no.
$:CCl_2+CH_2Cl_2 \leftrightarrow [C_2H_2Cl_4]^{\#} \rightarrow C_2HCl_3+HCl$	3.1E13	24.6	[24]	(28)
$:CCl_2+CH_3Cl \leftrightarrow [C_2H_3Cl_3]^{\#} \rightarrow C_2H_2Cl_2+HCl$	5.2E13	25.1	[24]	(29)
$:CCl_2+CH_4 \leftrightarrow [C_2H_4Cl_2]^{\#} \rightarrow C_2H_3Cl+HCl$	7.0E13	25.5	[24]	(30)

These chlorinated ethylenes convert to less chlorinated ethylene by H atom substitution reaction and H atom abstraction cyclic chain reactions. The chloroethylenes are dechlorinated by H addition displacement reactions, which are important channels for reducing the chlorine content of unsaturated chlorocarbons in sufficient hydrogen reaction system [6,19,27]. The H atom can add to C_2Cl_4 to form C_2HCl_4 radical as shown in reaction (31). The $[C_2HCl_4]^{\#}$ activated 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 π bond broken [12,13,28,29]. Prior to stabilization, it may dissociate back to reactants, become a stabilized radical or beta scission (radical simple unimolecular dissociation) to C_2HCl_3+ Cl via reaction (31). The other chloroethylenes ($C_2H_2Cl_2$ & C_2H_3Cl) are produced by a similar mechanism of C_2HCl_3 formation. Finally, the C_2H_4 as non-chlorinated hydrocarbon is formed by reaction (34).

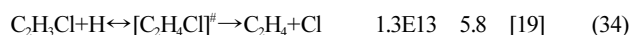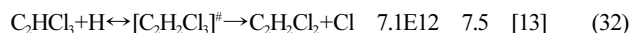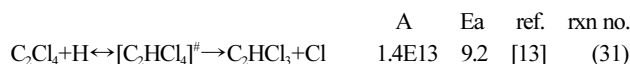|	A	Ea	ref.	rxn no.
$C_2Cl_4+H \leftrightarrow [C_2HCl_4]^{\#} \rightarrow C_2HCl_3+Cl$	1.4E13	9.2	[13]	(31)
$C_2HCl_3+H \leftrightarrow [C_2H_2Cl_3]^{\#} \rightarrow C_2H_2Cl_2+Cl$	7.1E12	7.5	[13]	(32)
$C_2H_2Cl_2+H \leftrightarrow [C_2H_3Cl_2]^{\#} \rightarrow C_2H_3Cl+Cl$	7.0E12	6.5	[19]	(33)
$C_2H_3Cl+H \leftrightarrow [C_2H_4Cl]^{\#} \rightarrow C_2H_4+Cl$	1.3E13	5.8	[19]	(34)

Fig. 9 summarizes the main reaction pathways for thermal decomposition of $CHCl_3$ with H_2 reaction atmosphere. This overall reaction scheme based on analysis of the observed products and thermochemical kinetics estimation is illustrated in Fig. 9. Non-chlorinated hydrocarbons and HCl as final products were formed by thermal hydrodechlorination under H_2 reaction atmosphere.
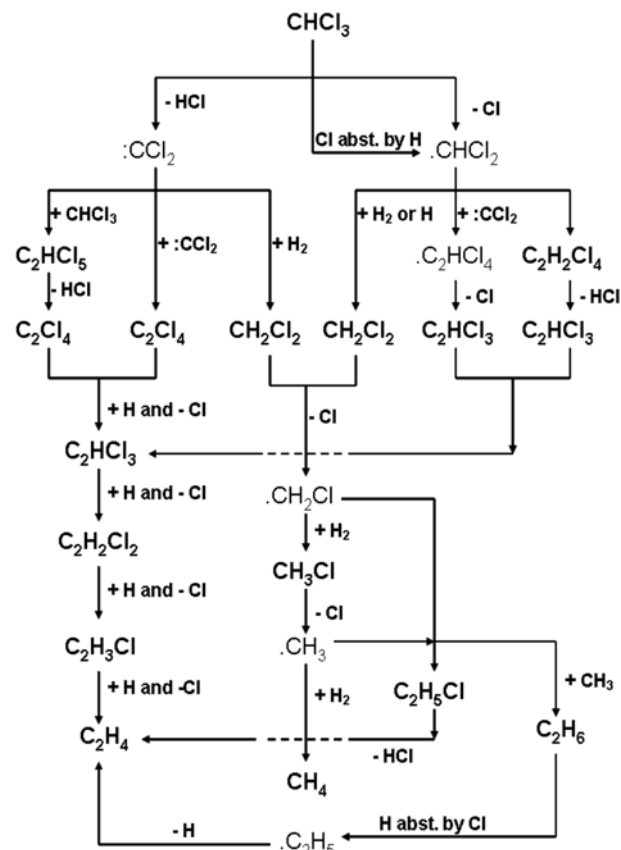
Fig. 9. Major reaction pathways for intermediate products in $CHCl_3/$ H_2 reaction system (Roles of H_2 for other product formation in $CHCl_3/H_2$).

CONCLUSIONS

Thermal reaction studies of diluted mixture (1%) of chloroform ($CHCl_3$) under argon (Ar) and hydrogen (H_2) reaction atmosphere have been investigated to examine the effect of reaction atmosphere on decomposition and product distribution. The experimental results were obtained over the temperature range 525-900 °C with reaction times of 0.3-2.0 sec at 1 atm by utilizing an isothermal tubular flow reactor. Complete destruction (>99%) of the parent reagent, $CHCl_3$, was observed near 675 °C under H_2 reaction atmosphere ($CHCl_3/H_2$ reaction system) and 700 °C under Ar reaction atmosphere ($CHCl_3/Ar$ reaction system) with 1 sec reaction time. The $CHCl_3$ pyrolysis yielded more conversion in H_2 atmosphere than in Ar atmosphere. Major products in $CHCl_3/Ar$ reaction system were C_2Cl_4, CCl_4, C_2HCl_3 and HCl over a wide temperature range. Hydrocarbon was not found in $CHCl_3/Ar$ reaction system. Major products of $CHCl_3/H_2$ reaction system observed were CH_2Cl_2, CH_3Cl, CH_4, C_2Cl_4, C_2HCl_3, $C_2H_2Cl_2$, C_2H_3Cl and HCl at 600 °C with 1 sec reaction time. Non-chlorinated hydrocarbons such as CH_4, C_2H_4 and C_2H_6 were the major products above 850 °C. Product distributions were distinctly different in Ar or H_2 reaction atmosphere. The H_2 gas plays a key role in acceleration of reagent decay and formation of non-chlorinated light hydrocarbons through hydrodechlorination process. The important reaction pathways, based on thermochemical and kinetic principles, to describe the features of reagent decay and intermediate formation under each Ar and H_2 reducing

reaction atmosphere, were investigated. The main reaction pathways for formation of major products along with preliminary activation energies and rate constants were suggested.

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