Thermal decomposition of trichloroethylene under a reducing atmosphere of hydrogen

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Abstract−The thermal reaction of trichloroethylene (TCE: C_2HCl_3) has been conducted in an isothermal tubular flow reactor at 1 atm total pressure in order to investigate characteristics of chlorinated hydrocarbons decomposition and pyrolytic reaction pathways for formation of product under excess hydrogen reaction environment. The reactions were studied over the temperature range 650 to 900 °C with reaction times of 0.3-2.0 s. A constant feed molar ratio $C_2HCl_3 : H_2$ of 4 : 96 was maintained through the whole experiments. Complete decay (99%) of the parent reagent, C_2HCl_3 was observed at temperature near 800 °C with 1 s reaction time. The maximum concentration (28%) of $C_2H_2Cl_2$ as the primary intermediate product was found at temperature 700 °C where up to 68% decay of C_2HCl_3 occurred. The C_2H_3Cl as highest concentration (19%) of secondary products was detected at 750 °C. The one less chlorinated methane than parent increased with temperature rise subsequently. The number of qualitative and qualitative chlorinated products decreased with increasing temperature. HCl and dechlorinated hydrocarbons such as C_2H_4, C_2H_6, CH_4 and C_2H_2 were the final products at above 800 °C. The almost 95% carbon material balance was given over a wide range of temperatures, and trace amounts of C_6H_6, C_4H_6 and C_2HCl were observed above 800 °C. The decay of reactant, C_2HCl_3 and the hydrodechlorination of intermediate products, resulted from H atom cyclic chain reaction via abstraction and addition replacement reactions. The important pyrolytic reaction pathways to describe the important features of reagent decay, intermediate product distributions and carbon mass balances, based upon thermochemical and kinetic principles, were suggested. The main reaction pathways for formation of major products along with preliminary activation energies and rate constants were given.

Key words: Thermal Decomposition, Pyrolysis, Trichloroethylene (TCE), Reaction Pathway

INTRODUCTION

Safe destruction of hazardous materials has become of major concern for environmental protection. Of particular importance are chlorinated hydrocarbons (CHCs), which are major constituents of many industrial wastes. Incineration represents a viable mode of disposal of CHCs, so understanding the combustion characteristics of CHCs and the effects CHCs on incineration is important [1]. CHCs are major industrial chemicals and common environmental pollutants. They are used in the production of refrigerants, as an extraction solvent in the manufacture of pharmaceuticals and rubber, and as a general solvent in plastic, dye, oil, wax, cleaning, and dry cleaning industries [2]. The thermal decomposition is of interest because it is not readily biodegraded and is a confirmed carcinogen [3].

The incineration can affect the total conversion of hazardous organic compounds to safe, innocuous, thermodynamically controlled, end-products, such as carbon dioxide and water, plus compounds like HCl, which may be easily scrubbed with existing pollution control equipment. In practice, total conversion to innocuous materials is not easily achieved without considerable effort, and with an incinerator of less than optimum design or operating conditions, stable components in the waste feed may not be totally decomposed [4].

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 incinera-

tion, the H-Cl is the strongest (thermodynamically) and has the lowest Gibbs free energy of formation per chlorine atom. HCl is, therefore, a thermodynamically favored product for chlorine, providing there exists sufficient hydrogen for its stoichiometric formation [5]. It is noted, however, that the O-H bond in water 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. Consequently, C-Cl 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. It is important to understand both their pyrolysis and oxidation [6,7].

One desired and thermodynamically favorable product from a chlorocarbon conversion process is HCl, providing there exists sufficient H_2. In oxidation, both oxygen and Cl compete for the available hydrogen fuel, and this is one reason why chlorocarbons serve as flame inhibitors [8]. To obtain a quantitative formation of HCl, as one of the desired and thermodynamically favorable products, from chlorocarbons, one might use a straightforward thermal conversion of these compounds under a reducing atmosphere of hydrogen. The chlorocarbon and hydrogen systems contain only the elements C, H and Cl, and are expected to lead to the formation of light hydrocarbons and HCl at the temperatures where complete reaction occur [9].

In this study, trichloroethylene (TCE: C_2HCl_3) was used as a model chlorocarbon system to investigate hydrodechlorination processes of chlorocarbons with excess hydrogen. This work has focused on intermediate product distributions and the reaction pathways to form

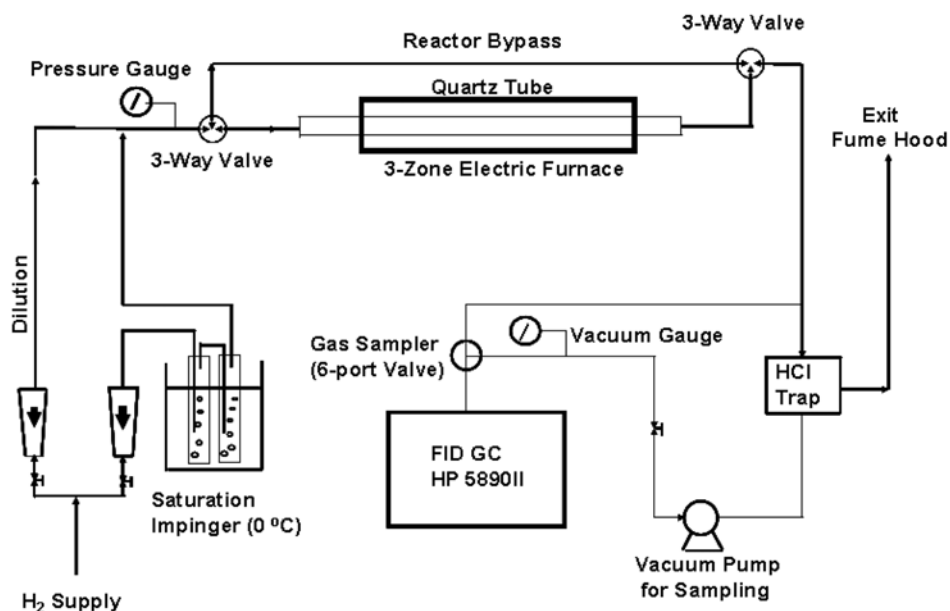†To whom correspondence should be addressed.
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Fig. 1. Schematic diagram of experimental system.

various products based on fundamental thermochemical and kinetic principles for pyrolytic C_2HCl_3 reaction with excess hydrogen. We characterize the reactant loss, intermediate product formation as functions of time and temperature to describe the reaction process, and to investigate the feasibility of the formation of the light hydrocarbons, e.g., CH_4 or C_2H_4 from the pyrolytic reaction of C_2HCl_3.

EXPERIMENTAL METHOD

Trichloroethylene (C_2HCl_3) was reacted with hydrogen (in the absence of O_2) in an isothermal tubular reactor at 1 atm. The products of such thermal degradation were analyzed systematically by varying the temperature from 525 to 900 °C and the residence time from 0.3 to 2.0 s. A diagram of the experimental system is shown in Fig. 1. Hydrogen gas was passed through a multi-saturator train held at 0 °C ice bath to insure saturation with C_2HCl_3 for accurate vapor pressure calculation. A second (dilutent) stream of hydrogen gas was used to achieve the desired mole fraction of 4% C_2HCl_3 that was maintained throughout a whole experiment. The reagent with hydrogen gas was fed continuously into tubular flow reactor in vapor phase. The mixture was preheated to about 200 °C before entering the reactor to improve isothermal temperature control. The reactor effluent was passed through heated transfer lines to the gas chromatograph sampling valves and exhaust. All gas lines to the analytical equipment were held at 170 °C to limit condensation. The quartz tube reactor of 8 mm ID was housed 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 by using a type K thermocouple probe moving coaxially within the reactor under steady state flow. Tight temperature control resulted in temperature profiles isothermal within ±3 °C over 75% of the furnace length for all temperature ranges of this study.

On-line GC (HP 5890 II) 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 was used to inject sample. Quantitative analysis of HCl was performed for each run. The samples for HCl analysis were collected independently 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.

RESULTS AND DISCUSSION

1. Experimental Product Distributions in C_2HCl_3/H_2 Reaction System

Fig. 2 presents the parent reactant, C_2HCl_3 decay and product distributions identified by GC analysis in a hydrogen excess environment. Carbon mol fractions of products relative to initial number
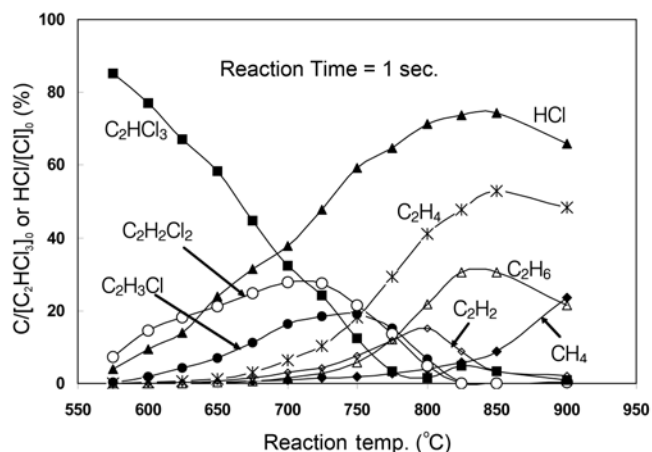

Fig. 2. Product distribution vs. temperature in C_2HCl_3/H_2 reaction system.

Table 1. Carbon mass balance in C_2HCl_3/H_2 reaction system (C_2HCl_3 : H_2=4 : 96, Reaction time=1 s)

| Species mole (%)	Reaction temperature (℃)										
	575	600	625	650	675	700	725	750	775	800	900
CH_4	ND	ND	0.3	0.4	0.6	1.0	1.4	1.9	2.8	3.9	23.6
C_2H_2	ND	ND	0.4	0.7	1.6	3.0	4.3	7.6	11.6	15.0	2.0
C_2H_4	0.1	0.3	0.5	1.2	2.9	6.4	10.3	18.2	29.3	41.2	48.3
C_2H_6	ND	0.1	0.1	0.3	0.6	1.5	2.7	5.9	12.2	21.9	21.3
C_2HCl	0.3	0.5	0.8	0.9	1.2	1.4	1.4	1.4	1.3	0.8	0.1
C_2H_3Cl	0.2	1.7	4.2	7.0	11.1	16.4	18.6	19.0	15.1	6.6	2.2
C_2H_5Cl	ND	0.1	0.2	0.4	0.5	0.5	0.5	0.4	0.2	ND	ND
CH_2Cl_2	ND	ND	ND	ND	0.2	0.3	0.4	0.3	0.2	0.1	ND
C_2Cl_2	ND	0.1	0.1	0.1	0.3	0.3	0.2	0.1	0.1	ND	ND
C_4H_6	ND	ND	ND	ND	0.3	0.6	1.0	0.9	0.7	0.4	0.1
CH_2CCl_2	7.1	14.4	18.0	21.0	24.8	27.8	27.4	21.5	13.5	4.7	0.3
CH_3CHCl_2	0.4	1.1	0.9	0.5	0.4	0.3	0.2	0.1	ND	ND	ND
$CHClCHCl$	0.8	1.8	2.4	2.9	3.5	3.7	3.0	2.0	0.9	0.2	ND
C_3H_5Cl	ND	ND	0.3	0.2	0.5	0.5	0.4	0.2	0.1	ND	ND
C_2HCl_3	85.3	76.9	67.1	58.5	44.6	32.4	24.2	12.4	3.4	1.2	0.4
C_6H_6	ND	ND	ND	ND	0.2	1.7	2.0	2.1	2.4	2.3	2.2
Total	94	97	95	94	93	98	98	94	94	99	100

ND: less than 0.1% carbon mole

of carbon mole of parent injected (C/C_o) are plotted versus reaction temperature at 1 s reaction time. Complete destruction (99%) of the C_2HCl_3 was observed at temperature near 800 ℃ with residence time 1 s. Major products observed were $C_2H_2Cl_2$, C_2H_3Cl and HCl at 675 ℃ where up to 50% decay of C_2HCl_3.

The formations of $C_2H_2Cl_2$ and C_2H_3Cl, as intermediate products increase proportionally to the decrease in C_2HCl_3 at below 700 ℃, strongly indicating that $C_2H_2Cl_2$ and C_2H_3Cl, are the initial stable products in a thermal reaction of C_2HCl_3 with H_2. The concentrations of $C_2H_2Cl_2$ and C_2H_3Cl drop quickly as temperature increases up to 825 ℃, where C_2H_4 increases. Formation of $C_2H_2Cl_2$ increases with increasing temperature to a maximum near 715 ℃ and then drops slowly. Formation of C_2H_3Cl also shows the same trend with one of $C_2H_2Cl_2$ but a maximum around 750 ℃. The C_2H_4 is then produced from further reaction of C_2H_3Cl with H_2 bath gas. In summary, the highest concentrations of intermediate products were observed at 715 ℃ for $C_2H_2Cl_2$, 750 ℃ for C_2H_3Cl and 850 ℃ for C_2H_4. The one less chlorinated ethylene than parent increased with temperature rise subsequently. This implies the less chlorinated ethylenes are more stable. It is consistent with the bond strengths of C-Cl bonds on chlorinated hydrocarbons which increase with decreasing chlorination [10]. The number and quantity of chlorinated products decrease with increasing temperature. Formation of non-chlorinated hydrocarbons, C_2H_4, C_2H_6, CH_4 and C_2H_2 increased as the temperature increased. The only non-chlorinated hydrocarbons were observed above 825 ℃. The formation of CH_4 increased rapidly above 850 ℃ where the C_2H_4 and C_2H_6 decreased. These reaction pathways based on experimental results and kinetics will be discussed in the next part.

The important hydrodechlorination processes of chloroethylenes result from H atom cyclic chain reaction by abstraction and addition replacement [11,12]. The overall reaction scheme based on prod-

uct distributions of the highest concentration chloroethylenes can be illustrated as follows:

$$C_2HCl_3 \xrightarrow[+H_2]{-Cl} C_2H_2Cl_2 \xrightarrow[+H_2]{-Cl} C_2H_3Cl \xrightarrow[+H_2]{-Cl} C_2H_4$$
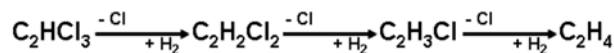
(plus HCl in each step)

Table 1 lists the carbon mass balance for products of C_2HCl_3 reaction system with temperature including minor products. The almost 100% carbon mass balances were given over a wide range of temperature. The various C_2 chlorinated hydrocarbons as main products were detected as shown in Table 2. The chlorinated hydrocarbons such as $C_2H_2Cl_2$, C_2H_3Cl, $C_2H_4Cl_2$ C_2HCl and C_2Cl_2 were observed at lower reaction temperature range. The formation of less chlorinated compounds increases with increasing temperature through the hydrodechlorination processes.

Small quantities of chlorinated acetylenes, C_2HCl and C_2Cl_2 were found over a wide temperature range, while the reagent, C_2HCl_3 was decomposed through double bond 4 member ring HCl elimination reaction, which has a relatively high energy barrier [7]. Also, small amounts chloroethanes, C_2H_5Cl and $C_2H_4Cl_2$ were detected at temperature between 575 and 750 ℃. The chloroethanes were decomposed to C_2H_4 and C_2H_3Cl via single bond 4 member ring HCl elimination reaction [13]. Benzene formation was observed above 675 ℃ where C_2H_2 concentration increased slightly from that at 625 ℃. The C_3 and C_4 products were also detected above 650 ℃.

Fig. 3 shows the product distribution in the pyrolysis of C_2HCl_3 as function of reaction time at 775 ℃ reaction temperature under excess hydrogen atmosphere. The formations of $C_2H_2Cl_2$ and C_2H_3Cl increase with a reaction time from 0 to 0.3 s, where C_2HCl_3 drops quickly. With reaction time rise, the $C_2H_2Cl_2$ and C_2H_3Cl decrease to be maximum around 0.3 s, and the formations of C_2H_4, C_2H_6 and C_2H_2 increase. Product distributions against reaction time as shown
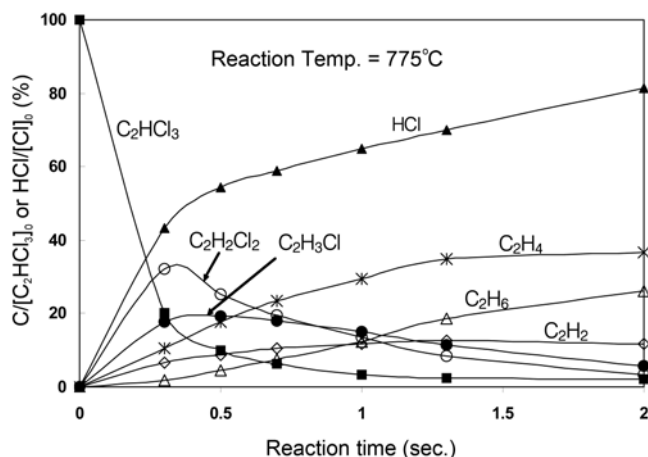
Fig. 3. Product distribution vs. temperature in C_2HCl_3/H_2 reaction system.

in Fig. 3 demonstrate similar trend to those against reaction temperature as shown in Fig. 2. The thermodynamically stable compounds, chloroethylenes, were destructed and hydrodechlorinated by H atom cyclic chain abstraction and addition replacement reactions [11,12].

2. Major Reaction Pathways for Products in C_2HCl_3/H_2 Reaction System

The reaction rate parameters of decomposition for C_2HCl_3 are listed in reactions (1a) and (1b). The unimolecular dissociation reactions are classified as simple dissociation (reaction (1a)) and complex dissociation (reaction (1b)). Transition State Theory [12,14] for a simple bond cleavage reaction (1a), estimates a loose configuration and Arrhenius A factor that is higher than the four center HCl elimination (1b) which has a tight transition state. However, the barrier height for HCl molecular elimination is sometimes lower than the simple bond cleavage [7,11]. The reaction rate constant for reaction (1b) at 700 is by 8 times faster that for reaction (1a). It is estimated that the only 0.1% decay of C_2HCl_3 by calculation based on rate constant ($k_{700\,°C}$) of reaction (1a) and (1b) may occur. However, big differences between calculation and experimental result are given. This indicates that there exist acceleration pathways for decomposition of C_2HCl_3. The discussion for the acceleration decay pathways of C_2HCl_3 will be as follows:

The initiation of acceleration for decay of C_2HCl_3 occurs due to Cl simple unimolecular dissociation of parent C_2HCl_3 to form active species, C_2HCl_2 radicals and Cl atoms by reaction (1a)). But on the other hand, reaction (1b) gives the stable species, C_2Cl_2 and HCl.

Table 2. Kinetic parameters for unimolecular decomposition of C_2HCl_3

Reaction	Reaction rate parameter				
	A	Ea	$k_{(700\,°C)}$	Source	rxn no.
$C_2HCl_3 \rightarrow C_2HCl_2 + Cl$	3.5×10^{15}	86.7	1.17×10^{-4}	[a,b]	(1a)
$C_2HCl_3 \rightarrow C_2Cl_2 + HCl$	5.3×10^{13}	74.4	1.02×10^{-3}	[a,b]	(1b)

A unit: (1/s) for unimoecular reaction, (cm³/mol·s) for bimolecular reaction
Ea unit: kcal/mol, k unit: mol/cm³·s

The C_2HCl_2 radical from reaction (1a) reacts with H_2 bath gas to produce primary product, $C_2H_2Cl_2$ as listed in reaction (4). As a result of thermochemical consideration [14], one may expect sufficient Cl atom concentration in C_2HCl_3 pyrolysis reaction system, because the C-Cl bond energy for C_2HCl_3 (89 kcal/mole) is lower than the C-H bond energy (110 kcal/mole) [7,15].

The acceleration for C_2HCl_3 decay results from the abstraction (3) by H of Cl from C_2HCl_3. The H atom is produced from reaction of Cl with H_2 bath gas like reaction (2). The Cl atom from initiation decay of C_2HCl_3 (reaction (1a)) reacts with H_2 to form H and HCl by reaction (2). The H atom accelerates decomposition of C_2HCl_3 by Cl abstraction reaction (3). In reaction (3), the H atom is consumed, but the H atom is produced via reaction (5). So, the H atom is not consumed apparently as listed in the overall reaction (5). The H cyclic chain reaction plays a catalytic role in the acceleration of C_2HCl_3 decomposition.

		A	Ea	source	rxn no.
$Cl + H_2$	$\rightarrow H + HCl$	4.8E15	5.0	[c]	(2)
$C_2HCl_3 + H$	$\rightarrow C_2HCl_2 + HCl$	3.6E12	9.2	[c,d]	(3)
$C_2HCl_2 + H_2$	$\rightarrow C_2H_2Cl_2 + H$	8.5E11	6.7	[c,e]	(4)
$C_2HCl_3 + H_2$	$\rightarrow C_2H_2Cl_2 + HCl$	(overall rxn (3) & (4))			(5)

These highly chlorinated ethylenes convert to less chlorinated ethylene by H atom addition displacement reaction and H atom abstraction cyclic chain reactions. Chloroethylenes are dechlorinated by H addition displacement reactions which are important channels for reducing the chlorine content of unsaturated chlorocarbons [7,11]. The H atom can add to C_2HCl_3 to form $C_2H_2Cl_3$ radical as shown in reaction (6). The $[C_2H_2Cl_3]^{\#}$ 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 [7,14]. Prior to stabilization, it may dissociate back to reactants, become a stabilized radical or beta scission (radical simple unimolecular dissociation) to $C_2H_2Cl_2 + Cl$.

$$C_2HCl_3 + H \leftrightarrow [C_2H_2Cl_3]^{\#} \rightarrow C_2H_2Cl_2 + Cl \qquad (6)$$
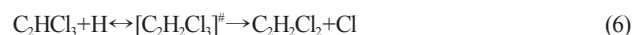
The decay of $C_2H_2Cl_2$ occurred due to Cl simple unimolecular dissociation of $C_2H_2Cl_2$ to form C_2H_2Cl radicals and Cl atoms as reaction (7). The C_2H_2Cl radical reacts with H_2 to produce C_2H_3Cl as listed in reaction (9). The other formation pathway of $C_2H_2Cl_2$ is Cl abstraction by H atom (reaction (8)). The H atom reacts with $C_2H_2Cl_2$ and rapidly forms HCl and C_2H_2Cl radical. The C_2H_2Cl radical then reacts with H_2 to regenerate H atoms and to produce a stable C_2H_3Cl molecule 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 C_2HCl_3 destruction (reaction (3) & (4)). The pathways for formation of C_2H_3Cl are similar to those for formation of $C_2H_2Cl_2$.

		A	Ea	source	rxn no.
$C_2H_2Cl_2$	$\rightarrow C_2H_2Cl + Cl$	9.3E15	86.6	[a,b]	(7)
$C_2H_2Cl_2 + H$	$\rightarrow C_2H_2Cl + HCl$	1.2E13	5.5	[c,f]	(8)
$C_2H_2Cl + H_2$	$\rightarrow C_2H_3Cl + H$	6.2E11	6.0	[a,g]	(9)
$C_2H_2Cl_2 + H_2$	$\rightarrow C_2H_3Cl + HCl$	(overall rxn of (8) & (9))			(10)

The C_2H_3Cl is produced from further reaction of $C_2H_2Cl_2$ via H addition reaction. The H atom addition reaction is important for reducing the chlorine contents of unsaturated chlorocarbons including aromatics [16,17]. This H addition reaction results in the formation of C_2H_3Cl and Cl atom through a Cl kick out reaction. The $C_2H_2Cl_2$ is decomposed similar to decomposition of C_2HCl_3.

$$C_2H_2Cl_2+H\leftrightarrow[C_2H_3Cl_2]^{\#}\rightarrow C_2H_3Cl+Cl \qquad (11)$$

The C_2H_4 as final product of this reaction system is also formed from further reaction of H abstraction cyclic chain reaction (13) & (14), and C_2H_3Cl via H addition displacement reaction (16). The C_2H_3Cl decay as illustrated in reactions (7)-(11) is explained by a similar mechanism of $C_2H_2Cl_2$ loss. Finally, the C_2H_4 as final non-chlorinated hydrocarbon is formed.

	A	Ea	source	rxn no.
$C_2H_3Cl \rightarrow C_2H_3+Cl$	4.0E15	91.7	[a,h]	(12)
$C_2H_3Cl+H \rightarrow C_2H_3+HCl$	1.0E13	6.5	[c,f]	(13)
$C_2H_3+H_2 \rightarrow C_2H_4+H$	5.0E11	7.3	[c]	(14)
$\overline{C_2H_3Cl+H_2 \rightarrow C_2H_4+HCl}$	(overall rxn (13) & (14))			(15)
$C_2H_3Cl+H\leftrightarrow[C_2H_4Cl]^{\#}\rightarrow C_2H_4+Cl$				(16)

The formation of C_2H_6 slowly increases at above 750 °C where the C_2H_4 increases as shown in Fig. 2. This indicates that the formation of C_2H_6 is associated with C_2H_4. The addition H to C_2H_4 occurs at a higher rate because of lower barrier to the addition [18], and results in C_2H_5. The C_2H_5 radical reacts with H_2 bath gas to produce C_2H_6 by reaction (18).

	A	Ea	source	rxn no.
$C_2H_4+H \rightarrow C_2H_5$	4.0E13	2.6	[i,j]	(17)
$C_2H_5+H_2 \rightarrow C_2H_6+H$	3.5E12	13.2	[c]	(18)

The formation of CH_4 rapidly increases at above 825 °C where the C_2H_6 decreases. This indicates that the initiation for formation of CH_4 results from decomposition of C_2H_6 (reaction (19)). The C-C bond energy for CH_3CH_3 (89 kcal/mole) is lower than the C-H bond energy (98 kcal/mole) [14]. The formation of CH_3 radical is thermodynamically favorable over one of C_2H_5+H. Also, the reaction (19) can occur in a high temperature range, even though it has a relatively high energy barrier [9]. The CH_3 radical reacts with H_2 bath gas to produce CH_4 by reaction (20).

	A	Ea	source	rxn no.
$CH_3CH_3 \rightarrow CH_3+CH_3$	7.9E16	89.4	[i,k]	(19)
$CH_3+H_2 \rightarrow CH_4+H$	3.3E12	12.5	[c]	(20)

Small quantities of C_2HCl were detected over a whole reaction temperature range (650-900 °C), while the reagent, CH_2CCl_2 was decomposed through 4 member ring HCl elimination reaction (1b) as described in earlier. Another reaction pathway for formation of C_2HCl is reaction (3), and the C_2HCl is formed from further reaction of CH_2CCl via β scission (21).

From Fig. 2, the C_2H_2 increases with increasing temperature to a maximum near 800 °C and then drops quickly. C_2H_2 was produced from 4 member ring HCl elimination of C_2H_3Cl (reaction (22)) and β scission of C_2H_3 (reaction (23)) [14,18].
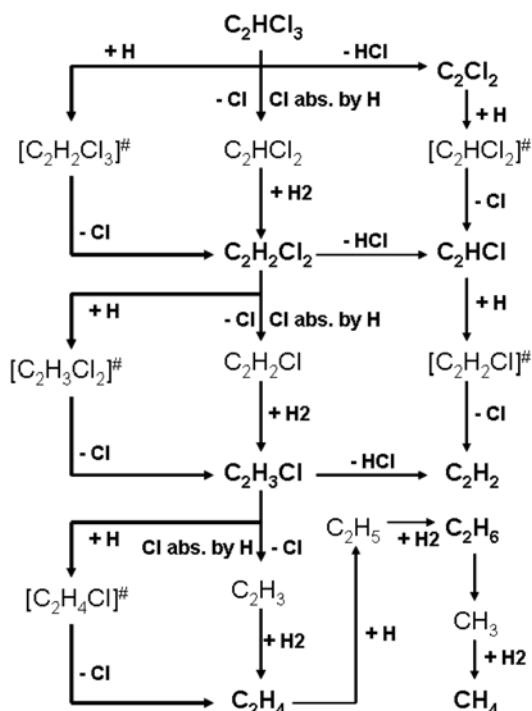

Fig. 4. Outline of important reaction pathways for intermediate products in C_2HCl_3/H_2 reaction system.

	A	Ea	source	rxn no.
$CH_2CCl_2 \rightarrow C_2HCl+HCl$	1.1E14	69.1	[a,b]	(1b)
$CH_2CCl_2+H \rightarrow CH_2CCl+HCl$	1.2E13	5.5	[c,d]	(3)
$CH_2CCl \rightarrow C_2HCl+H$	6.2E12	38.5	[b,g]	(21)
$C_2H_3Cl \rightarrow C_2H_2+HCl$	5.3E13	68.7	[g,h]	(22)
$C_2H_3Cl+H \rightarrow C_2H_3+HCl$	1.0E13	6.5	[c,f]	(23)
$C_2H_3 \rightarrow C_2H_2+H$	1.6E12	38.3	[b,j]	(24)

Formations of benzene and chlorobenzene were observed above 750 °C, where C_2H_2 known as the precursor of benzene increases slightly from that at around 725 °C and then decreases as more benzene is formed, as listed in Table 1. The unsaturated molecules begin to condense, leading ultimately to high molecular structure, aromatics or soot in pyrolysis [16,19].

Fig. 4 summarizes the main reaction pathway to form hydrodechlorinated products from C_2HCl_3. This overall reaction scheme based on analysis of the observed products and thermochemical kinetics estimation is illustrated in Fig. 4.

CONCLUSIONS

The thermal decomposition of C_2HCl_3 in H_2 bath gas was studied to investigate important chlorocarbon reaction pathways under pyrolytic atmosphere. The reactions were studied in an isothermal tubular reactor at a total pressure of 1 atm with reaction times of 0.3-2.0 s between 650 and 900 °C. Complete destruction (99%) of the C_2HCl_3 was observed at temperature near 800 °C with residence time 1 s. The formations of $C_2H_2Cl_2$ and C_2H_3Cl, as intermediate products increased proportionally to the decrease in C_2HCl_3 at below 700 °C. The one less chlorinated methane than parent increased with

temperature rise subsequently. Formation of non-chlorinated hydrocarbons, C_2H_4, C_2H_6, CH_4 and C_2H_2 increased rapidly at above 800 ℃. The main formation pathways for hydrodechlorinated products resulted from H atom cyclic chain reactions by abstraction and addition replacement. Product distributions along with preliminary activation energies and rate constants were given. The important pyrolytic reaction pathways to describe the important features of reagent decay, intermediate product distributions and carbon mass balances, based upon thermochemical and kinetic principles, were suggested. The results of this work provide a better understanding of pyrolytic decomposition processes which occur during the pyrolysis of C_2HCl_3 and similar chlorinated hydrocarbons.

ACKNOWLEDGEMENT

SOURCES OF KINETIC PARAMETERS IN REACTION PATHWAYS

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