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Thermal Decomposition Mechanism of Chlorinated Volatile Organics at Pyrolytic and Oxidative Conditions

Jong-In Dong† **and Kyoon-Duk Yoon**

Department of Environmental Engineering, The University of Seoul, 90 Jeonnong-dong, Seoul 130-743, Korea

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Abstract – Chlorinated hydrocarbons have been widely utilized due to their excellent physical properties and stability as solvents, coolants, propellants or raw materials etc. One of major problems in disposing of them is safe destruction or collection of recyclable components. One of most feasible methods for waste chlorinated organics is thermal treatment. In this study, experimental and theoretical analyses have been tried to investigate several fundamental operating parameters including temperature, residence time and background conditions like existence of oxygen. Vinyl chloride and trichloroethylene (TCE) were tested to observe their reaction mechanism. Vinyl chloride started to decompose at 725 °C, and 99 % of initial amount was decomposed at 830 °C, 1 sec in pyrolytic environment, produing C_2H_2 and HCl mainly and C_2HCl, C_2H_4, H_2 as byproducts depending on experimental conditions. TCE, on the other hand, produced C_2Cl_2, C_2Cl_4, HCl at pyrolytic conditions and CO and CO_2 additionally through COCl radical reactions at oxidative conditions. The supply of oxygen lowered the destruction temperature of TCE and C_2Cl_4 could be considered as an indirect indicator of TCE decomposition.

Key words : Thermal Decomposition, Pyrolysis, Vinyl Chloride, Trichloroethylene

INTRODUCTION

Wastes or residues of chlorinated hydrocarbons from industrial processes and domestic use have caused wide environmental problems because of the rapid increase of their utilization and a lack of treatment facilities [Pausteinbach, 1990]. Fifteen (15) halogenated compounds including trichloroethylene are classified as specific wastes (one type of industrial waste) in Korea [Whang et al., 1995].

Various treatment technologies have been introduced; however, thermal treatment/destruction methods have been accepted as the most feasible alternatives. For this purpose, the pyrolysis technique is used to convert the volatile compounds into useful hydrocarbons and hydrogen chloride through dehalogenation under reducing environment. On the other hand, the incineration method converts the compounds into low energy potential materials like CO_2, H_2O, and HCl [Gerber, 1985].

Special consideration should be given to treat hazardous wastes containing chlorine to prevent the generation of secondary air pollutants. Compounds containing less hydrogen than chlorine usually result in incomplete combustion or may have adverse effect to reduce OH radicals which are important in combustion reactions. The supply of excessive oxygen may drive the reaction to complete combustion; however, the lack of hydrogen can cause intermediate products like oxichlorinated carbons, which are precursors of dioxin, PCB and phosgene [Won, 1993].

In this study, the reaction mechanism and characteristics of vinyl chloride and trichloroethylene were investigated in pyrolytic and oxidative reaction conditions.

EXPERIMENTAL METHODS

A schematic diagram of the experimental equipment is given in Fig. 1. Operating parameters like reaction temperature, retention time and oxygen concentrations were varied. Argon was used as a bath gas to supply the reactants at constant levels. Oxygen was supplied by 5 % for the oxidative reactions. A quartz tube with 10 mm ID, 450 mm length was used as a reactor, which is considered to have neglectable wall effect.

Thermal decomposition experiments were performed at temperatures in the range of 700-900 °C for pyrolytic conditions, and 450-750 °C for oxidative conditions. Retention time ranged from 0.2 to 2.0 sec.

The concentrations of the reactants were controlled at their saturated vapor pressure by bubbling the bath gas through the 2

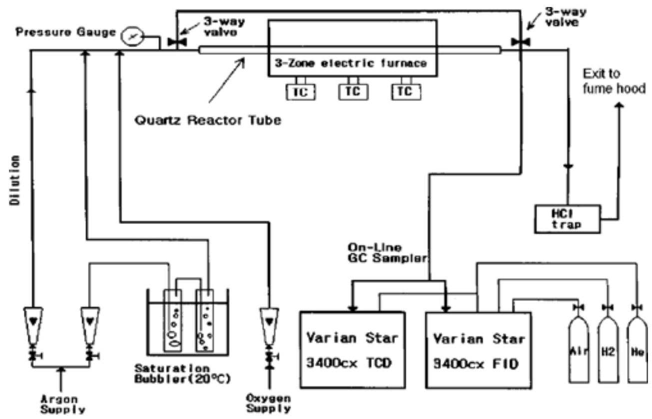

Fig. 1. Schematic diagram of experimental apparatus.

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†To whom correspondence should be addressed.
E-mail : jidong@uoscc.uos.ac.kr

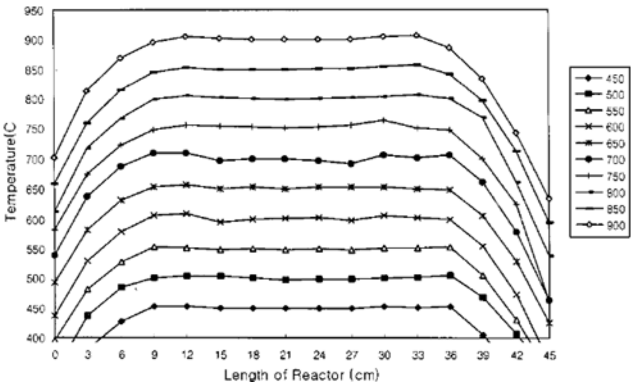

Fig. 2. Temperature profiles of the reactor.

sets of impinger kept in a 20 °C water bath. The concentration of vinyl chloride or TCE was adjusted by adding Ar gas, and oxygen was supplied and controlled at constant concentration. The reaction time was estimated from the effective reactor volume and the total gas flow rate of Ar gas, dilution gas and oxygen.

Inside temperature of the reactor was controlled by using independent PID-type temperature controllers. The temperature distribution was monitored by inserting K-type thermocouples into the reactor every 3 cm along the length, and the temperatures were controlled within ±3 °C of set values. Fig. 2, which shows the temperature distributions measured at different experimental conditions, shows a uniform temperature over 70 % of the reactor length.

The concentrations of the reactants and products were analyzed using on-line GC (Varian star 3400cx FID, TCD). The column for the FID detector GC was 1 % AT-1000 on Graphic GB (60/80 mesh) and that for TCD GC for CO and CO_2 was Molesieve 5A (60/80 mesh). The qualitative identification for final products was performed using GC/MS (Fision MD 800), and hydrogen chloride was analyzed using a titration method.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Summary of Experimental Results

The test results for 0.5 % vinyl chloride are summarized in Fig. 3, which depicts the product distribution for various temperatures at pyrolytic condition. On the other hand, Fig. 4 shows vinyl chloride conversion ratio for different reaction temperatures. For 1 sec reaction time, the decomposition is considered slow up to 725 °C and its rate increases fast as the temperature increases higher than this value.

The decomposition ratio of 99.99 % was accomplished at 850 °C at 2 sec, 875 °C at 1 sec and 900 °C at 0.6 sec. Fig. 5 shows the product distribution for various reaction times at constant temperature condition.

The test results of vinyl chloride decomposition with oxygen from the other set of experiments showed that 46.9 % was decomposed at 725 °C and 1 sec (11.9 % decomposition at no oxygen condition) while 77.7 % was decomposed at 775 °C (42.3 % at no oxygen condition).

When the reaction time was changed, the decomposition rate change at oxidative condition was more significant than that at pyrolytic condition. The decomposition rate was also accelerated (46.9 to 90 %) with oxygen ratio increase (0.05 to 1).

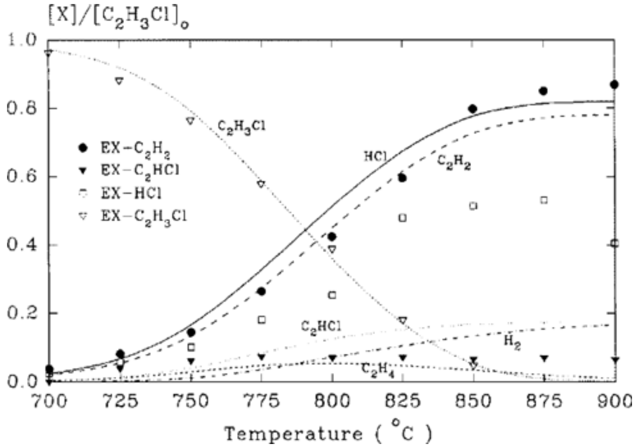

Fig. 3. Conversion and product distribution vs. temperature for vinyl chloride at 1 sec average retention time.
(EX means experimental data and solid lines show predicted concentrations using Chemkin)

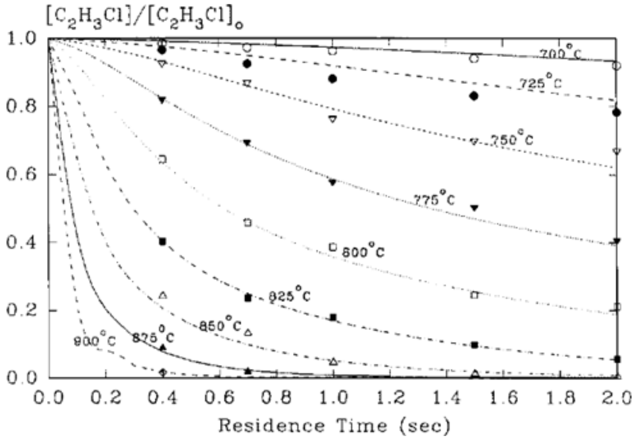

Fig. 4. Conversion vs. time for vinyl chloride at different temperatures.
(Points show experimental data and solid lines show predicted concentrations using Chemkin)

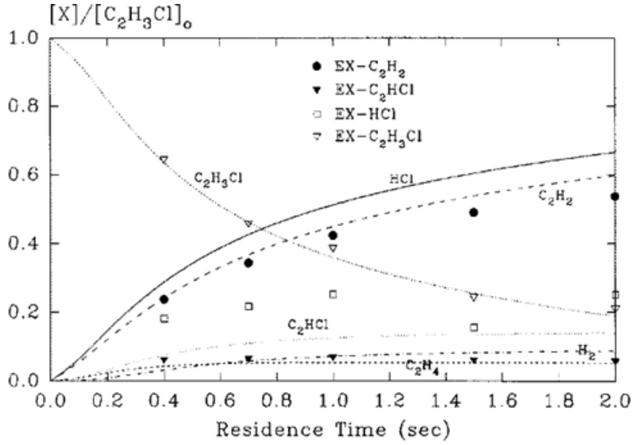

Fig. 5. Product distribution for vinyl chloride decomposition vs. reaction time at 800 °C.

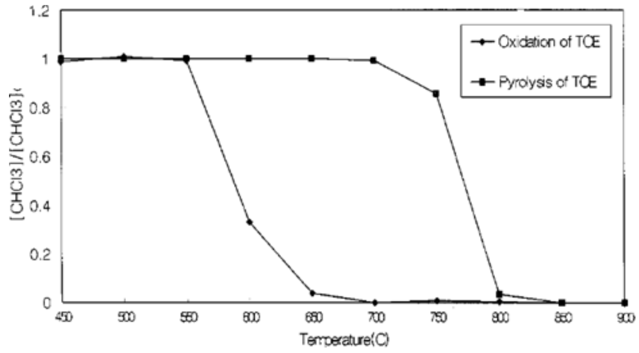

Fig. 6. Comparison of TCE decomposition vs. temperature at pyrolytic/oxidative environments.

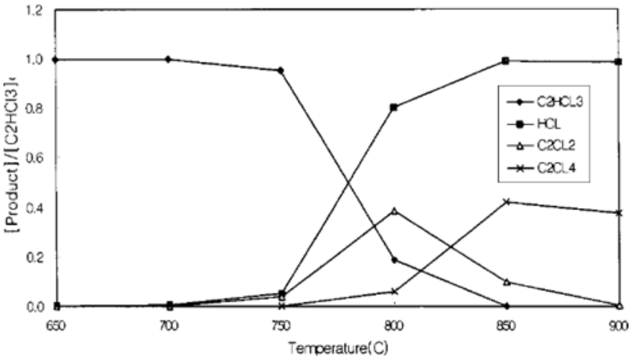

Fig. 7. Major species profiles for TCE decomposition at different temperature at pyrolytic environment.

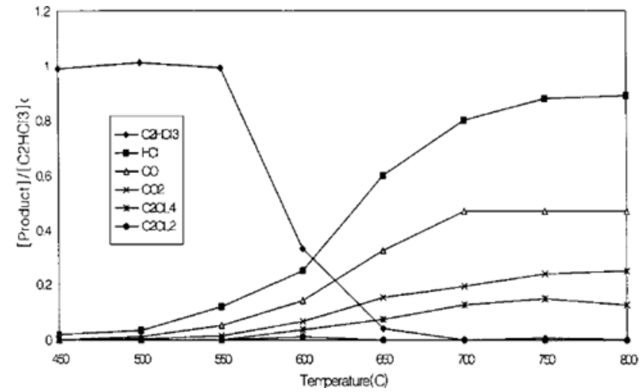

Fig. 8. Major species profiles for TCE decomposition at different temperature at oxidative environment.

The test results of pyrolysis and oxidative decomposition of trichloroethylene are summarized in Fig. 6 in terms of decomposition ratio. The decomposition started to occur at 730 °C at pyrolytic conditions; however, it occurred at 560 °C at oxidative condition, which is considered as a result of the acceleration effect of oxi-radicals to decompose the TCE molecules.

Fig. 7 and 8 show product distribution for TCE reaction at pyrolytic and oxidative conditions by temperature change at 1 sec of reaction time. At the pyrolytic condition, main initial product was HCl and intermediate product was C_2Cl_2, which tends to convert to C_2Cl_4.

In oxidative reaction case, the initial product was HCl; however, the intermediate compound C_2Cl_2 was hardly observed and C_2Cl_4 was also detected at low level as their decomposition occurs at the early stage. Oxidative products CO and CO_2 could be observed by substantial amount. When the results were analyzed as in the figures, C_2Cl_4 could be considered as an indirect indicator of TCE thermal decomposition both in pyrolytic and oxidative reactions.

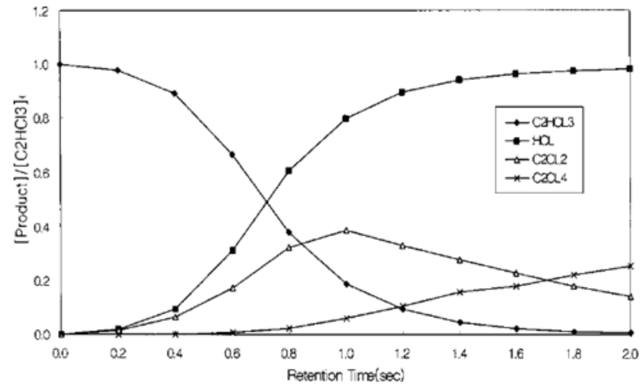

Fig. 9. Major species profiles for TCE decomposition at different retention time at pyrolytic environment.

When the pyrolytic reaction of TCE proceeds, the product distribution could be changed as shown in Fig. 9. The main product is C_2Cl_2 at initial stage and then C_2Cl_4 becomes more dominant product, which shows a series reaction characteristics of TCE.

2. Analysis of Reaction Mechanism

2-1. Initiation Reaction of TCE

Unimolecular initiation decomposition of TCE may be divided into simple dissociation and complex dissociation of 4-member ring HCl removal reaction. One of its major reaction may be expressed as below.

For the reaction temperature of 750 °C, the reaction constant of HCl removal reaction (2) is faster by about 100 times than Cl removal reaction (1); however, C-Cl bond energy is large due to the C-C double bond of chloroethylene. The main decomposition mechanism is, therefore, abstraction and addition reaction of active compound like Cl radical. The decomposition rate of unimolecular dissociation reaction is very low when estimated using reaction rate constants; therefore, C_2HCl_3 is considered to be decomposed mainly through bimolecular decomposition reactions.

Reactions	Forward reaction rate parameters			
	A (1/sec)	E (cal/mole)	k (at 750 °C)	Rxn no.
$C_2HCl_3 \rightarrow C_2HCl_2 + Cl$	1.0E15	91,000	3.6×10^{-5}	<1>
$C_2HC1_3 \rightarrow C_2Cl_2 + HCl$	3.2E13	74,400	4.08×10^{-3}	<2>
$C_2HCl_3 + Cl \rightarrow C_2Cl_3 + HCl$	1.0E15	91,000	3.6×10^{-5}	<3>

Because C_2HCl_3 gas limited amount of hydrogen and it is consumed continuously by the reactions shown below, Cl becomes an important radical in the bimolecular reactions. This can be observed in Fig. 7 and the following figures where HCl is formed from the early stage of the reaction and the reaction rate like reaction (3) is very fast.

$$RCl+H \leftrightarrow R+HCl \tag{4}$$

$$Cl_2+H \leftrightarrow HCl+Cl \tag{5}$$

$$HCl+H \leftrightarrow H_2+Cl \tag{6}$$

2-2. Pyrolytic Decomposition of TCE

The main products of pyrolytic decomposition of TCE are HCl and C_2Cl_2 as shown in Fig. 3 (reaction time of 1 sec), which is summarized below. This product distributions are discussed in initiation reactions.

$$C_2HCl_3 \leftrightarrow C_2Cl_2+HCl \tag{7}$$

$$C_2HCl_3+Cl \leftrightarrow C_2Cl_3+HCl \tag{8}$$

$$C_2Cl_3+M \leftrightarrow C_2Cl_2+Cl+M \tag{9}$$

$$C_2Cl_3+Cl_2 \leftrightarrow C_2Cl_4+Cl \tag{10}$$

$$C_2Cl_3+Cl \leftrightarrow C_2Cl_4 \tag{11}$$

C_2Cl_2 molecules started to form about 730 °C, at which temperature TCE decomposes, and showed a maximum peak at about 800 °C, then decreased as the temperature increased. As C_2Cl_2 concentration decreased, that of C_2Cl_4 started to increase. C_2Cl_3 radicals formed by reaction (3) contribute to produce C_2Cl_4 as shown in reactions (10) and (11), which decreases C_2Cl_2 level.

2-3. Oxidation Reactions of TCE

The important intermediate product C_2Cl_2 in pyrolytic reactions could not be observed at significant levels in oxidation conditions, which may be explained as follows.

There are not enough data for the reaction rate between O_2 and C_2Cl_2 produced by reactions (7) and (9). The reaction rate between chloro-acetylene and oxygen is known to be relatively fast [Smirnov et al., 1967]. This reaction could be estimated very fast when reaction rate was calculated by transition-state theory [Benson, 1976; Moore 1972; Dean and Bozzelli, 1991].

As the reaction (12) is faster than reaction (9), trichlorovinyl radicals (C_2Cl_3) formed when C_2HCl_3 is decomposed do not have main reaction exit channel to C_2Cl_2 like the case in pyrolytic decomposition, but to COCl radicals which are important to form CO and CO_2.

The main products were, therefore, CO and CO_2 and they started to form at 550 °C at 1 sec reaction time, at which temperature TCE started to decompose. COCl radicals formed in reaction (12) and (13) are converted into CO molecules and they again react with ClO, resulting in the formation of CO_2 [Chang et al., 1996; Taylor and Tirey, 1994].

$$C_2Cl_2+O_2 \leftrightarrow COCl+COCl \tag{12}$$

$$C_2Cl_3+O_2 \leftrightarrow COCl_2+COCl \tag{13}$$

$$COCl+M \leftrightarrow CO+Cl+M \tag{14}$$

$$COCl+O_2 \leftrightarrow CO_2+ClO \tag{15}$$

$$COCl+Cl \leftrightarrow CO+Cl_2 \tag{16}$$

$$CO+ClO \leftrightarrow CO_2+Cl \tag{17}$$

CONCLUSIONS

Various experiments have been performed to observe the thermal decomposition and reaction behavior of hazardous chlorinated ethenes (vinyl chloride and trichloroethylene) both in pyrolytic and oxidative conditions. Fundamental operating parameters including temperature, residence time and background conditions like existence of oxygen were tested at lab-scale experimental apparatus to obtain basic insights into reaction patterns at different conditions.

Vinyl chloride started to decompose at 725 °C, and 99 % of the initial amount was decomposed at 830 °C, 1 sec in pyrolytic environment, producing C_2H_2 and HCl mainly and C_2H-Cl, C_2H_4, H_2 as byproducts depending on experimental conditions. TCE, on the other hand, produced C_2Cl_2, C_2Cl_4, HCl at pyrolytic conditions and CO and CO_2 additionally through COCl radical reactions at oxidative conditions, in which case C_2Cl_2 showed relatively low concentration. The supply of oxygen lowered the destruction temperature of TCE and C_2Cl_4 could be considered as an indirect indicator of TCE decomposition.

REFERENCES

Benson, S. W., "Thermochemical Kinetics," 2nd Ed. John Wiley Son (1976).

Chang, W. D., Karra, S. B. and Senkan, S. M., "A Detailed Mechanism for the High Temperature Oxidation of C_2HCl_3," *Combustion Sci. and Tech.*, **49**, 107 (1996).

Dean, A. M. and Bozzelli, J. W., "CHEMACT-A Computer Code to Estimate Rate Constants for Chemically-Activated Reactions," *Combustion. Sci. and Tech.*, **80**, 63 (1991).

Gerber, C. R., "EPA's Hazardous Waste Research Programs," *J. Air Pollution Control Assoc.*, **35**, 749 (1985).

Moore W., "Physical Chemistry," 4th Ed., Prentice-Hall (1972).

Pausteinbach, D. J., "The Risk Assessment of Environment and Human Health Hazards," John Wiley & Sons (1990).

Smirnov, K. M., Tomilov, A. D. and Shchekotikhin, A. I., "Haloacetylenes," *Russian Chem. Rev.*, **36**, 326 (1967).

Taylor, P. H. and Tirey, D A., "Detailed Modeling of the Pyrolysis of Trichloroethylene: Formation of Chlorinated Aromatic Species," *Combustion Sci. and Tech.*, **101**, 75 (1994).

Whang, J. S., Lee, C. T. and Lee, H. G., "Introduction to Waste Treatment," Munjisa (1995).

Won, Y. S., "Reaction Mechanism of Pyrolytic Decomposition of Dichloromethane/111-Trichloroethane Mixture in Excess Hydrogen; II. Detailed Reaction Mechanism Modeling," *J. of Korean Society of Environmental Engineers*, **15**(5), 675 (1993).