Numerical Simulations of the Pyrolysis of 1, 2 Dichloroethane

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Numerical simulations of 1, 2 dichloroethane(EDC) pyrolysis are conducted to understand the process in the production of the vinyl chloride monomer(VCM) and by-products. A chemical kinetic mechanism is developed, with the adopted scheme involving 44 gas-phase species and 260 elementary forward and backward reactions. Detailed sensitivity analyses and the rates of production analysis are performed on each of the reactions and the various species, respectively. The concentrations of EDC, VCM, and HCl predicted by this mechanism are in good agreement with those deduced from experiments of commercial and laboratory scale. The mechanism is found to accurately predict the EDC yield and the production of by-products by varying the ranges of pyrolysis temperature, residence time, and pressure which impact on the pyrolysis of 1, 2 dichloroethane. The influence of reactions related to H atom on the relative sensitivity of EDC becomes important as the residence time increases. The pyrolysis of EDC mainly occurs through $C_2H_4Cl_2+Cl=CH_2ClCHCl+HCl$.

Key Words : 1, 2 Dichloroethane, Pyrolysis, Vinyl Chloride Monomer, Residence Time, Sensitivity Analyse, Chemical Kinetic Mechanism

1. Introduction

The vinyl chloride monomer (VCM) is the very important basic raw material to manufacture PVC (poly vinyl chloride) used for a wide variety of purposes in the industry, the formation of which is mainly achieved through the process of 1, 2 dichloroethane (ethylene dichloride or EDC) pyrolysis. Many studies on the decomposition of EDC have been worked under the thermal decomposition [Barton, 1949; Barton and Howlett, 1949; Howlett, 1952; Holbrook *et al.*, 1971, Ranzi *et al.*, 1992; Incavo, 1996], the catalysed pyrolysis by chlorine or other species [Ashmore *et al.*, 1982a; Ashmore *et al.*, 1982b], and the photolysis [Yano and Tschulkow-Roux, 1980; Ma *et al.*, 1990; Cardy *et al.*, 1993].

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The thermal decomposition is one of the most widely used methods in commercial processes for the production of vinyl chloride. Commercially the decomposition of EDC is performed in EDC cracking reactors at temperatures of 773-823 K and at pressures of 25-30 atm in order to reduce reactor size, to improve heat transfer, and to separate better HCl from the product VCM [McPherson *et al.*, 1979]. The conversion of EDC to VCM is generally kept in 50-60% range. The undesirable by-products such as acetylene, ethylene, methyl chloride, butadiene, vinyl acetylene, benzene, chloroprene, other chlorinated hydrocarbons, etc. [McPherson *et al.*, 1979], are generated during the precesses of EDC pyrolysis, some of which have potentially toxic properties. So a better understanding of the pyrolysis of EDC through detailed studies of elementary reactions to VCM production is of considerable practical importance. Detailed knowledge of the reaction paths helps to optimize production processes. It reduces the formation of by-products that have a serious impact on environmental health. It is cost

-intensive to remove them from the product cycle. The understanding of the elementary steps in the decomposition of EDC leads to a better control of the emission of pollutants like soot, higher molecular weight products, hydrogen chloride, etc..

Barton(1949) carried out 1, 2 dichloroethane pyrolysis in addition of small amount of oxygen or chlorine with clean-walled glass tubular reactors. The influence of these traces species greatly increased the decomposition rate of highly purified 1, 2 dichloroethane. Barton and Howlett (1949) reported that the decomposition of 1, 2 dichloroethane happened in the temperature range 635-758K by a nearly homogeneous, first-oder reaction to give vinyl chloride and hydrogen chloride. Howlett(1952) suggested the following radical-chain mechanism of thermal decompostion of 1, 2 dichloroethane.

(1) $C_2H_4Cl_2 \rightarrow C_2H_3Cl + Cl$,
    $k_1 = 1 \times 10^{13} \ exp(-70000/RT)$
(2) $Cl + C_2H_4Cl_2 \rightarrow C_2H_3Cl_2 + HCl$,
    $k_2 = 4.17 \times 10^8 \ exp(-5000/RT)$
(3) $C_2H_3Cl_2 \rightarrow C_2H_3Cl + Cl$,
    $k_3 = 1 \times 10^{10} \ exp(-22000/RT)$
(4) $Cl + C_2H_4Cl \rightarrow C_2H_3Cl + HCl$,
    $k_4 = 1 \times 10^{10} \ exp(-3000/RT)$

With the steady state approximation, the rate of the global reaction was shown as $k = 6.46 \times 10^{10} \ exp(-47000/RT)$ provided that $k_2[C_2H_4Cl_2] > k_3$. Holbrook *et al.* (1971) performed the pyrolysis of 1, 2 dichloroethane in reaction vessels coated with pyrolytic films in conditions with the temperature (613-788K), surface/volume ratio (1.32−37.4 cm^{-1}), and initial pressure (4× 10^{-4}−0.4 atm). For the pyrolysis at low surface/ volume ratio, a modified Howlett mechanism including the wall reaction was suggested through more detailed study of the reaction mechanism in reactors of different surface/volume ratio. Ranzi *et al.* (1992) presented simulation results of the pyrolysis of 1, 2 dichloroethanein with the kinetic scheme coupled with a furnace model and appropriate mathematical techniques. The model was used as a starting point for the study of different reacting systems both in terms of design of new

reactors for EDC pyrolysis and in terms of the evaluation of the effect of possible additives, typically chlorinated hydrocarbons. Incavo (1996) performed the analysis of 1, 2 dichlorethane pyrolysis with a gas chromatographic pyrolysis device, and presented the influence of conversion parameters such as pyrolysis temperature and residence time on product distribution including the minor or trace species.

The current study describes numerical predictions of EDC pyrolysis with the detailed chemical reaction mechanism that is validated with experimental results to be found in the literature. Detailed sensitivity analyses are performed on each of the reactions in the mechanism in order to investigate their influence on reactant destruction and product formation. This enables recognition of the important reactions influencing the decomposition of EDC and the major pathways of product formation. The rates of production (or destruction) analysis for the various species included in the mechanism are executed in order to determine the contribution of each reaction to the net production or destruction rate of a species. The EDC yield and the production of by-products are investigated by varying the ranges of parameters, such as pyrolysis temperature, residence time, and pressure, which impact on the pyrolysis of EDC.

2. Numerical Approach

Numerical simulation of the decomposition of EDC are performed using the previously developed computer code, Aurora computer program[Meeks *et al.*, 1998] (Chemkin-III Version 3.5 from Sandia National Laboratories). The code allows calculations of the decomposition of EDC using a detailed mechanism of chemical reactions as well as a thermodynamic properties of chemical species. The thermodynamic properties of species as inputs of the computer code are part of the reacting system in a standard format [Kee *et al.*, 1990], and such data are available [Kee *et al.*, 1990]. Those species not available in

Table 1 All species considered and some reactions of the detailed chemical kinetic mechanism used in the numerical simulations

Species considered in the system

$C_2H_4Cl_2$	CH_2ClCH_2	$CH_2ClCHCl$	CH_2CHCl	$CHClCHCl$
C_2HCl_3	CH_2CCl_2	HCl	C_2H_4	C_2H_2
CH_4	C_2H_3	C_2H_5	C_2H_6	CH_2
CH_3	H	H_2	Cl	Cl_2
CH_2Cl	C_2H_5Cl	C_2H	CH_3Cl	$CHCl_3$
$CHCl_2$	CCl_3	CCl_2	C_2Cl_4	CCl_4
CH_2Cl_2	$CHCl$	$C_2H_3Cl_3$	CH_3CHCl_2	CH_3CHCl
$CHCl_2CHCl$	CH_2ClCCl_2	$CH_2(S)$	$CHClCCl$	C_2Cl_3
C_2HCl	C_2Cl_2	CH	C_2Cl_5	

No[*]	REACTIONS	$(k = A\ T^{**}b\ \exp(-E/RT))$			Source
		A	b	E	
		(cm-mol-s)		(cal/mol)	
1.	$C_2H_4Cl_2 = CH_2ClCH_2 + Cl$	1.00E+13	0.00	70000.0	a
4.	$C_2H_4Cl_2 + Cl = CH_2ClCHCl + HCl$	2.97E+13	0.00	2160.0	a
6.	$C_2H_4Cl_2 + H = CH_2ClCHCl + H_2$	5.00E+13	0.00	10000.0	b
9.	$CH_2ClCHCl = CH_2CHCl + Cl$	1.00E+13	0.00	21000.0	c
10.	$CH_2ClCHCl + Cl = CHClCHCl + HCl$	2.00E+13	0.00	0.0	d
32.	$CH_2CCl_2 + H = CH_2CHCl + Cl$	7.21E+12	0.00	7510.0	e
34.	$CHClCHCl + H = CH_2CHCl + Cl$	3.44E+13	0.03	5890.0	e
57.	$CH_2Cl + CH_2Cl = C_2H_4Cl_2$	3.92E+45	-10.21	13200.0	e
96.	$C_2H_4 + Cl = C_2H_3 + HCl$	1.00E+14	0.00	7000.0	e

Note:
a : Howlett(1952)
b : Bozzelli, J.W.(1995)
c : Barton and Howlett(1949)
d : Leylegian et al.(1998)
e : Miller(1995)
[*] : The reaction number based on the detailed chemical kinetic mechanism [Lee, 2000]

the database are given from NIST Chemistry WebBook and Leyegian et al. (1998).

The thermal decomposition of EDC has been studied previously under homogeneous conditions with characteristics of a chain reaction [Howlett, 1952]. The reaction mechanism suggested by Howlett(1952) is reported, as seen in (1) - (4). However, it becomes generally known that this mechanism is sufficient at low conversion rather than at high conversion of EDC related to the performances of commercial units. It is observed that the conversion of EDC happens at very low (less than 1%) when this mechanism is used with Barton's condition [Barton, 1949] at temperature of 773K and at pressure of 1 atm.

We have developed a detailed chemical kinetic mechanism which is given primarily from Miller (1995) and are added partilly from a wide range of sources [Howlett, 1952; Bozzelli, 1995; Barton and Howlett, 1949; Leylegian et al., 1998]. This mechanism, which is reported elsewhere [Lee, 2000], includes 260 elementary forward and backward reactions, and involves 44 gas-phase species. A list of these species is to be found in Table 1. Table 1 reports only a small subset of reactions that are important on the relative sensitivity of EDC, VCM, and HCl.

3. Results and Discussion

3.1 Validation of the mechanism and comparison with experimental results

With the kinetic mechanism developed the EDC conversions are calculated in conditions of constant temperature (848K) and reactor volume (3.475×10^{-1} cm^3) [Incavo, 1996] with respect to residence time, the results of which are represented in Fig. 1. There is excellent agreement between the numerical predictions and experimental results from Incavo(1996) for the case of residence time = 1 sec. As the residence time increases, the EDC conversion in calculation shows a little higher than that in experimental results. The reason for the discrepancy between calculation and experimental results is unclear. One source of error can be attributed to experimental errors, and another to errors in the kinetic mechanism of Table 1. Whatever the source is, both set of results are in good agreement in the whole range of residence time. In case of the production of VCM, both calculation and experimental results are in excellent agreement in the whole range of residence time.

Figure 2 shows the mole fraction of EDC, VCM, and HCl with respect to reactor temperature in condition of pressure at 10 atm and for the last 8 m of total tube length (280 m) where temperature remains constant [Ranzi et al., 1992]. The calculated EDC conversion is about 55 %, as shown in Fig. 2, at temperature of 753K, the result of which is in an excellent agreement in compared with commercial data (55 %) [Ranzi et
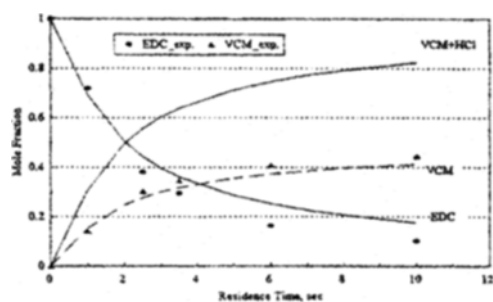
Fig. 1 The mole fraction of EDC, VCM, and HCl with respect to residence time at constant temperature and reactor volume. Line : numerical results, symbols : experimental results (Incavo, 1996)
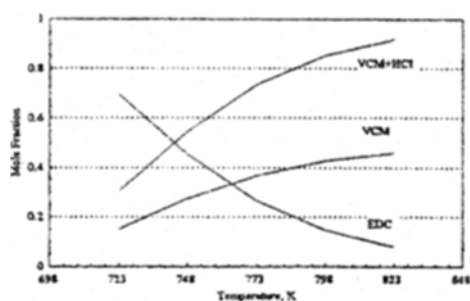

Fig. 2 The mole fraction of EDC, VCM, and HCl with respect to reactor temperature

Fig. 3 The mole fraction of EDC, VCM, and HCl with respect to reactor pressure

veloped are relatively in good agreement with the results of experiments performed with the condition of commercial or laboratory scale.

3.2 The analyses of sensitivity

A sensitivity analysis is performed for reactor condition corresponding to a value of residence time $= 1$ and 10 sec in order to determine the relative influence of individual reactions on the species' concentration. In Fig. 4, results are presented for the relative sensitivity of the pyrolysis of EDC $(C_2H_4Cl_2)$ to individual reactions; reactions for which a relative sensitivity of less than | 1% | with respect to the pyrolysis of EDC and the production of VCM or HCl is predicted are not reported. In terms of their influence, some reactions are more important than others, such as reactions R1, R4, R9, R10, and R57 for residence time $= 1$ sec, the rates of which should require accurate determination. The most important reactions of these are R1 and R9 which include chlorine atom as species producted when $C_2H_4Cl_2$ and $CH_2ClCHCl$ are decomposed. Secondly the reactions, R4 and R10, which product HCl through the consumption of chlorine atom, are important. In case of residence time $= 1$ sec, the sensitivity analysis reveals that reactions related to the production of HCl and the production or the consumption of Cl play very important role in the pyrolysis of EDC.

For reactions as stated above, the relative sensitivity of EDC has higher value in condition of residence time $= 10$ sec than in residence time $= 1$ sec. In addition, another reactions, R6, R32, and R34, for which a relative sensitivity of more than

al., 1992]. It shows that the reaction mechanism can predict the conversion of EDC even though in commercial condition. The EDC conversion is very sensitive on the a variation of reactor temperature. The increase of reactor temperature leads to increasing the rate of the pyrolysis of EDC in reactor, and of the production of VCM and HCl. It is shown that the reactor temperature plays an important role in the pyrolysis of EDC.

Figure 3 represents the mole fraction of EDC, VCM, and HCl with respect to reactor pressure in commercial condition. As the reactor pressure is increased from a value of 10 atm to 14 atm, the rates of the pyrolysis of EDC as well as of the production of VCM and HCl increase. However, on the conversion of EDC, the influence of reactor pressure is very much less than that of reactor temperature.

As discussed above, the results of numerical simulation with the reaction mechanism de-
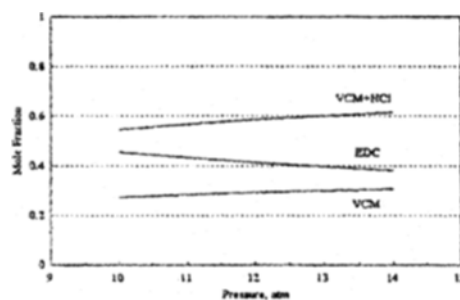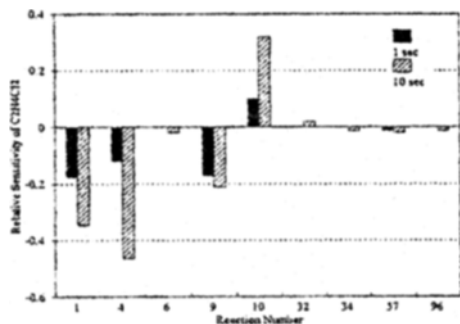
Fig. 4 The relative sensitivity of $C_2H_4Cl_2$ for some significant reactions in case of residence time = 1 and 10 sec
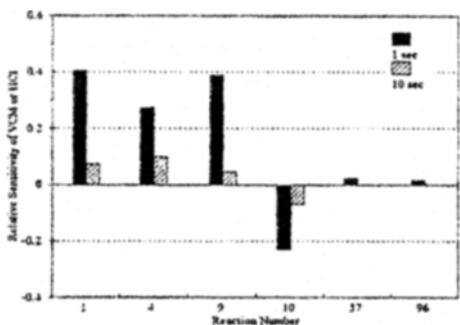

Fig. 6 Schematic diagram of the pathways of EDC pyrolysis for residence time = 1 sec

Fig. 5 The relative sensitivity of VCM or HCl for some significant reactions in case of residence time = 1 and 10 sec

Fig. 7 The mole fraction of major by-products (C_2 H_2, CH_3CHCl_2, $CHClCHCl$, and C_2H_4) with respect to residence time at constant temperature and reactor volume

| 1% | with respect to the pyrolysis of EDC is predicted appear, each of which include H atom. As the residence time increases, the influence of reactions related to H atom on the relative sensitivity of EDC becomes important.

Figure 5 presents the relative sensitivity of the production of VCM or HCl to the significant reactions. The results of numerical simulation for the relative sensitivity show the same for the production of VCM and HCl. Reactions, R1, R4, R9 and R10, on the influence of the relative sensitivity of EDC also effect on the relative sensitivity of VCM or HCl. As the residence time increases, the magnitude of the relative sensitivity of important reactions decreases.

3.3   The rate-production

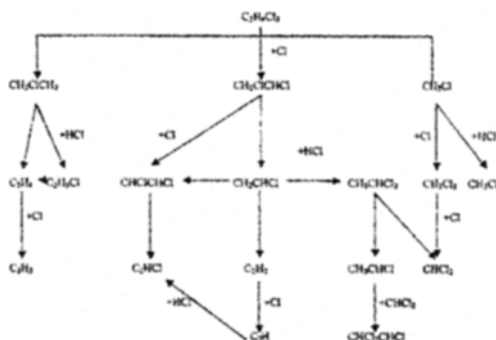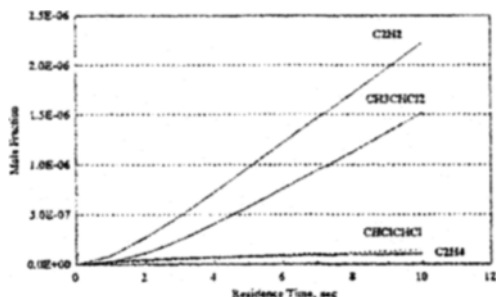This study examined the rate of consumption and formation of every species in the context of

each reaction with the option of rate of production analysis in Aurora [Meeks *et al.*, 1998]. Figure 6 shows a schematic diagram of the consumption of EDC pathways in case of residence time = 1 sec. A great portion of the pyrolysis of EDC occurs through formation of $CH_2ClCHCl$ that influences formation of VCM (CH_2CHCl). The pyrolysis of EDC has alternative pathways to the formation of CH_2ClCH_2, $CH_2ClCHCl$, and CH_2Cl, but their portion for the rate of consumption of EDC is very insignificant. The consumption of $CH_2ClCHCl$ occurs to formation of VCM by the extraction of chlorine atom. The major portion of HCl is produced when EDC reacts with chlorine atom (R4) to generate CH_2 $ClCHCl$.

It is shown that $CHClCHCl$, C_2H_2, and CH_3 $CHCl_2$ among minor species (which are the rest of species in except EDC, VCM, and HCl) are the primary by-products, the amount of which are

steadily increased as the residence time is increased, as shown in Fig. 7. The production of them except C_2H_4 occurs through the consumption of VCM whereas the production of C_2H_4 does through the consumption of CH_2ClCH_2 and C_2H_5Cl.

4. Conclusions

The detailed chemical reaction mechanism for the pyrolysis of EDC is developed and validated with experimental results found in the literature. Detailed sensitivity analyses are performed on each of the reactions in the mechanism and the rates of production (or destruction) analysis for the various species included in the mechanism are executed. These enable recognition of the important reactions influencing the decomposition of EDC and the major pathways of product formation. The EDC yield and the production of by-products are investigated by varying the ranges of parameters, such as pyrolysis temperature, residence time, and pressure, which impact on the pyrolysis of EDC.

(1) The detailed chemical kinetic mechanism for the pyrolysis of EDC is developed, which consists of 260 elementary forward and backward reactions, and involves 44 gas-phase species. The results of numerical simulation with this mechanism are in good agreement with the experimental results performed with the condition of commercial or laboratory scale.

(2) As a result of a detailed sensitivity analysis, several important reactions (i.e., R1, R4, R9 and R10) are identified. As the residence time increases, the influence of reactions related to H atom on the relative sensitivity of EDC becomes important.

(3) The pyrolysis of EDC mainly occurs through $C_2H_4Cl_2 + Cl = CH_2ClCHCl + HCl$. The amount of the primary by-products is steadily increased as the residence time is increased.

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