Kinetics of the Uninhibited Reaction of 2-Chloropropene-Part II: Comparison with Inhibited Reaction

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Summary: The kinetics of the uninhibited reaction of 2-chloropropene in the gas-phase has been studied between 662 and 747 K at pressures ranging from 11 to 76 Torr with the object of determining the overall mechanism using static system. The reaction was found to be accurately of the first order at the high pressures and the observed rate coefficient is expressed by the following Arrhenius equation:

$k_{total} \Rightarrow uninhibited \Rightarrow = 10^{7.98 \, \pm \, 0.6} \, (s^{-1}) \, exp^{-167 \, \pm \, 7.8 \, (kJ/mole)/RT}$

The activation energy was calculated at 167 ± 7.98 kJ/mol and identified with the dissociation of C-Cl bond. The reaction is presumed to be unimolecular at lower temperature with formation of propyne and elimination of hydrogen chloride. However, at high temperature C-Cl bond fission takes place and this changes the mechanism of the reaction. Two mechanisms dehydrohalogenation molecular elimination and C-Cl bond fission are discussed.

Keywords: Gas-phase kinetics; Static system; 2-chloropropene; Uninhibited reaction; Mechanism; C-Cl bond fission.

Introduction

Works on the thermal gas phase kinetics of unimolecular reaction in the low temperature region 500-700 K have been of great interest over the last three decades. There have been numerous experimental techniques by which a molecule can thermally energize. Among these the heating the reactants in gas phase in pyrex reactors have been most popular. Static reactor technique coupled with gas chromatography has become standard tools for studying chemical kinetics at low temperature [1]. This procedure allows determining the high pressure rate constant for various reactions. It also allows estimating and correcting the contribution to the rate parameters due to surface effect. Renewed interest in this technique is mainly due to much needed kinetics data at low temperature 500-700 K for those reaction mixtures whose high temperature kinetics over the temperature range 900-1200 K have been determined using single pulse shock tube apparatus.

There have been several studies of the kinetics of the gas phase decomposition of halogenated hydrocarbons using thermal activation techniques over temperature range of 550 – 750 K and these have been reviewed. All the studies have been directed to establish the mechanism of various classes of compounds. Majority of these reactions which have been studied seem to take place by way of four-centre and six-centre cyclic activated complex. Large portion of the four-centre reactions

are hydrogen halide eliminations from the alkyl halides to produce olefins [2, 3]. The only experimental thermal results on HX elimination from unsaturated hydrocarbons are those for hydrogen chloride and hydrogen bromide elimination from vinyl chloride and bromide [4, 5]. This compound was previously investigated in a static system in the presence of an inhibitor [6]. The objectives of the present work is to investigate the kinetics and mechanism of the gas phase thermal decomposition of 2-chloropropene in the absence of an inhibitor under conventional static system conditions using seasoned reactors and to compare the results with the earlier study. The rate constants for the reaction were determined over a wide range of temperatures and pressures. The Arrhenius rate expression was established for the reaction. The study will help to extend the existing data base on the kinetics of halogenated hydrocarbons.

Experimental

2-chloropropene (98%, boiling point 22.5–22.8°C) was purchased from ACROS and tested for impurities by Gas Chromatography. Standard hydrocarbons gases used were of Matheson Company.

The static system for thermal activation studies includes a vacuum line, the reaction vessels

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and the salt bath [7]. The whole of the vacuum line was made up of Pyrex glass tubing. A manometer was constructed in between the line for measuring the exact pressure of the sample taken for analysis. A pirani head (Edwards Pirani 1001) was connected to the vacuum line through a ground glass joint. The vessels containing the liquid samples were maintained at ⌃ 0°C in a Dewar flask filled with ice cold water.

Reaction vessels were imbedded in molten salt thermostat, with a temperature accuracy of ⌫1°C by Honeywell DC 1010 temperature controller. The bath was heated by a heater made up 8 meters length and outer diametre of 5.7 mm of stainless steel sheathed heating cable around the inside of the can. This was very suitable for maintaining temperature of up to 750 K. However, for higher temperature studies an auxiliary heater was also used in combination with the main heater. Temperature was measured with a K-type thermocouple. The molten salt was stirred with a steel stirrer driven by a motor (Universal Electric Co.). This allowed the even distribution of the heat within the bath. Prior to any kinetic experiment, the pressure in the reactor was reduced to about 10^{-3} mm of Hg by a high vacuum pumping system Model VPC-050 (Sinku Kiko Co., Ltd. Yokohama, Japan).

Analyses were made by Shimadzu Gas Chromatograph fitted with 6-port gas sampling valve, pre-packed Porapak Q column and flame ionization detector. The following chromatographic conditions were used for the analysis of the products obtained as a result of pyrolysis: The column oven temperature was programmed at the rate of 32 °C/min in the temperature range 70 – 170 °C with nitrogen as carrier gas at flow rate of 23 mL/min. Injection port temperature was kept at 170 °C. The products were identified by comparing the retention time of the peaks of standards with those of sample.

Results and Discussion

Uninhibited Reaction

This reaction has been studied over the temperature range 668 – 747 K with pressures varying between 11 – 76 Torr without using any inhibitor. It was observed that at relatively high temperature the plot of log [unreacted 2-chloropropene] versus the reaction time plot was hardly linear up to 3% conversion. Beyond that limit it becomes flattened or scattered and no linearity is observed as shown in Fig. 1. In order to minimize this problem the majority of kinetic runs were limited

to a maximum of 3 – 4% reaction. There were 2 – 5 fold decreases in rate after 5 minutes at high temperatures. This behaviour though present is less pronounced at lower temperatures. This means at high temperatures C-Cl bond fission takes place resulting into the formation of Cl radical as
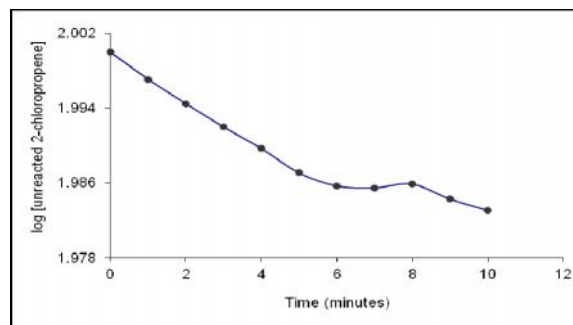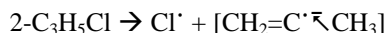
$$2\text{-}C_3H_5Cl \rightarrow Cl^{\cdot} + [CH_2=C^{\cdot}\diagdown CH_3]$$

Fig. 1: The non-linear behaviour beyond 3% conversion for the loss of 2-chloropropene at 727.2 K.

The result is an increase in the rate of radical chain initiation with respect to chain propagation. As a consequence of this, higher radical concentration is built up which increases the termination rate vis-à-vis propagation rate. This behaviour was also observed by Dai *et al*. [8] during the study of unimolecular reactions of chloroalkanes by IR laser pyrolysis. First order rate plot for this reaction at 727.2 K is shown in Fig. 2. The rate constant expression derived from the Arrhenius plot for this reaction is as

$$k_{\text{total}} \Rightarrow \text{Uninhibited} \Rightarrow = 10^{7.98} {}^{\pm 0.6} \; (s^{-1}) \exp^{-167} {}^{\pm 7.8}_{(kJ/mole)/RT}$$
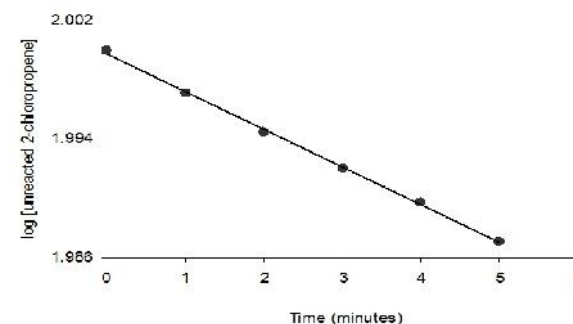
All error limits in this work are 95% certainty limits.

Fig. 2:   First order rate plot for the loss of 2-chloropropene at 727.2 K for the uninhibited reaction.

Comparison of Uninhibited and Inhibited Reaction

Combined first order rate plot and Arrhenius plot for the uninhibited and inhibited reactions are shown in Fig. 3 and 4. It can be seen from Fig. 4 that it is much more difficult to make the reaction to proceed after more than 3 % conversion without using inhibitor. Secondary product reactions become important in this region. Huybrechts and co-workers [9] observed such behaviour during the pyrolysis of 1,1,1-trichloroethane in the presence and absence of added HCl. They termed this behaviour as self-inhibition at higher conversion. Using 1% n-hexane as inhibitor controls such an abnormal behaviour. The reaction proceeds for longer period with four-fold increase in conversion. This means the radicals formed are successfully trapped by n-hexane.
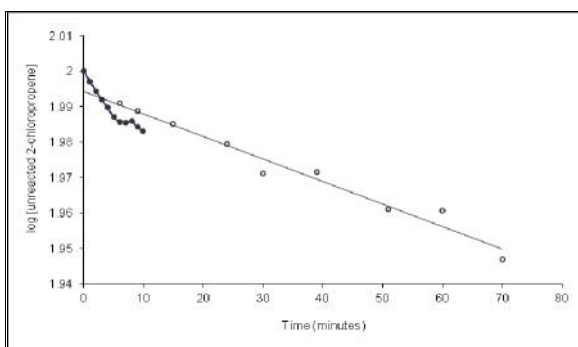

Fig. 3:   A combined first order rate plot for the loss of 2-chloropropene at 727.2 K. Filled circles are for uninhibited reactions and open circles for inhibited reaction with 1% n-hexane.
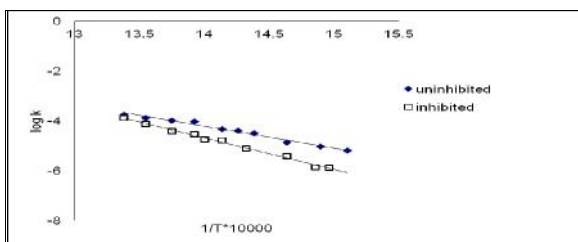

Fig. 4:   A combined Arrhenius plots for thermal decomposition of uninhibited and inhibited reaction. Closed diamonds are for uninhibited reaction and open squares denote reaction with 1% n-hexane.

Mechanisms

Thermal decomposition of 2-chloropropene is, from a mechanistic point of view, a complex reaction. Large effect of inhibitor on the rate of reaction clearly indicates that the decomposition involves free radicals, initiated by the fission of C-Cl bond. Following reaction scheme summarizes the reaction pertinent to the present study   [10-12].

(a). $C_3H_5Cl \rightarrow [CH_2=C^\bullet-CH_3] + Cl^\bullet$ (chain initiation)
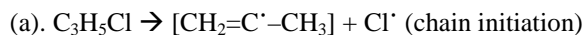
The chlorine atom produced as a result of C-Cl bond fission is certainly, a good reactant and in this specific environment will remove a hydrogen atom from 2-chloropropene resulting into the formation of $^\bullet C_3H_4Cl$ radical and hydrogen chloride [12].

(b). $Cl^\bullet + C_3H_5Cl \rightarrow {}^\bullet C_3H_4Cl + HCl$ (chain propagation b,c,d,e steps)
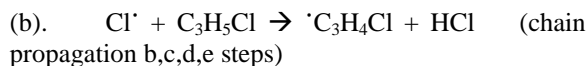
At this high temperature C-Cl bond fission takes place, chlorine radical is produced

(c). $^\bullet C_3H_4Cl \rightarrow C_3H_4 + Cl^\bullet$

which in turn react with $^\bullet C_3H_4Cl$ to form propyne and chlorine molecule. The resultant accumulation of chlorine molecules, exert an initiating action on the decomposition of 2-chloropropene [9,10] and thus autocatalysis occurs owing to the accumulation of chlorine molecules as depicted in reactions (d) and (e).

(d). $^\bullet C_3H_4Cl + Cl^\bullet \rightarrow C_3H_4 + Cl_2$
(e). $Cl_2 + {}^\bullet C_3H_5 \rightarrow C_3H_4 + Cl^\bullet + HCl$
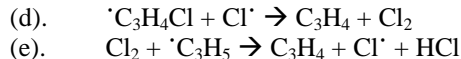
We also presume that chain termination takes place at a chlorine atom and this assumption is in accord with literature [11].

(f). $Cl^\bullet + wall \rightarrow \Rightarrow Cl^\bullet \Rightarrow$ (f, g, chain termination)
(g). $Cl^\bullet + Cl^\bullet \rightarrow Cl_2$
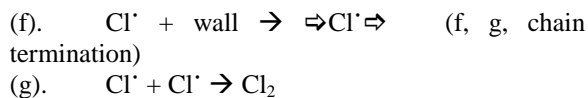
Hauser and Bernstein [13] also used almost the same type of mechanism during the pyrolysis of pentachloroethane. A summary of these reactions with supporting references is given in Table-1 [6, 11-13]. The fact that for an uninhibited reaction initially the rate is high but decreases substantially when the reaction is preceded for longer period, shows the dominance of the initiation process over the propagation process at this stage and as such the termination rate increases resulting into the slowing down of the reaction. This increase in rate at the initial stage gives lower value of activation energy and pre-exponential factor to the reaction. A comparison of the Arrhenius parameters for dehydrohalogenation reactions of certain chlorinated compounds having almost similar activation energies and pre-exponential factors as observed in case of our uninhibited reaction are given in Table-2 [6, 11, 14].

Table-1: Summary of proposed reactions from the pyrolysis of 2-chloropropene with supporting references.

Reaction	References
1. Molecular reaction: 2-ClC$_3$H$_5$ → propyne + HCl	6
2. Elementary radical reaction steps: (a). C$_3$H$_5$Cl → ⇨CH$_2$=C·–CH$_3$⇨ + Cl·	this study & 12, 13
(b). Cl· + C$_3$H$_5$Cl → ·C$_3$H$_4$Cl + HCl	12
(c). ·C$_3$H$_4$Cl → C$_3$H$_4$ + Cl·	this study
(d). ·C$_3$H$_4$Cl + Cl· → C$_3$H$_4$ + Cl$_2$	this study
(e). Cl$_2$ + ·C$_3$H$_5$ → C$_3$H$_4$ + Cl· + HCl	this study
(f). Cl· + wall → ⇨Cl·⇨	11
(g). Cl· + Cl· → Cl$_2$	11

Table-2: Comparison of Arrhenius parameters from dehydrohalogenation reaction of certain chlorinated hydrocarbons.

Reaction	Temperature/K	logA/s^{-1}	Ea/kJ mole^{-1}	References
CHCl$_2$CCl$_3$·C$_2$Cl$_4$+HCl	697-721	11.6	167.1	11
CH$_2$=CHCH$_2$Cl·allene+HCl	643-748	10.1	192.06	14
2-C$_3$H$_5$Cl·propyne+HCl	662-747	13.05	242.56	6
2-C$_3$H$_5$Cl·⇨CH$_2$=C·–CH$_3$⇨ + Cl·				
Cl· + C$_3$H$_5$Cl → ·C$_3$H$_4$Cl + HCl				
·C$_3$H$_4$Cl → C$_3$H$_4$ + Cl·				
·C$_3$H$_4$Cl + Cl· → C$_3$H$_4$ + Cl$_2$	662-747	7.98	166.94	this study
Cl$_2$ + ·C$_3$H$_5$ → C$_3$H$_4$ + Cl· + HCl				
Cl· + wall → ⇨Cl·⇨				
Cl· + Cl· → Cl$_2$				

Conclusion

Pyrolysis of 2-chloropropene is, from a mechanistic point of view, a complex reaction. The decomposition involves free radicals, initiated by C-Cl bond fission. The activation energy was calculated at 167±7.98kJ/mol and identified with the dissociation of C-Cl bond. Initially the rate was observed to be high and decreased substantially when the reaction proceeds for longer period, showing the dominance of the initiation process over the propagation process and as such the termination rate increases resulting into the slowing down of the reaction.

Acknowledgement

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