Kinetics Study of Dehydrohalogenation of 1-chlorohexane

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Summary: Thermal decomposition of 1-chlorohexane was studied over temperature range 623 - 833 K and pressure between 5-20 Torr. Following rate expression was obtained for homogeneous, non-radical dehydrohalogenation reaction.

$k_{(total)} = 10^{9.84\pm 1.08}\ s^{-1} \exp^{-177.25\pm 3.55\ (kJ/mole)/RT}$

The observed activation energy and frequency factor was found to be consistent with the elimination of hydrochloric acid via four-member cyclic transition state. The effect of the surface on the reaction was studied at 653.2 K using the packed reaction vessel. It was observed that the reaction proceeds 10 % faster in the packed vessel than the unpacked reaction vessel. The effect of pressure on the reaction was investigated at 653.2 K. A series of 10 minute's pyrolysis with initial pressure in the range 5-20 torr were made. There was Ca. 10.3 % increase in the rate of reaction as the pressure was lowered from 20 to 5 Torr.

Introduction

Halogenated hydrocarbons are widely used in chemical industry through out the world both as end products and as precursors for the manufacture of a wide variety of useful products including plastics, polymers, solvents, pesticides, refrigerants, fire retardant and other products. Attempts to understand and model the chemistry associated with the production, disposal and environmental fates of chlorinated and brominated hydrocarbons require the reliable kinetics and thermodynamic values for these compounds [1-3]. Such data are critical inputs in fundamental reaction models that are used to understand and control reaction efficiencies and pathways in chemical system [4-8].

Due to importance of chlorinated and brominated hydrocarbons in combustion and environment, efforts are on, for the last several decades to study the kinetics of thermal decomposition of these compounds. Maccoll [9] observed that there are three processes by which the pyrolysis of organic bromides occurs. Firstly, direct elimination of hydrogen bromide takes place, secondly, breaking of C-Br bond occurs which lead to production of a bromine atom and thirdly, the bromine atom participates in the propagation of chain reaction. Maccoll studied allyl bromide in the temperature range of 320-380 °C and found out that the reaction is homogeneous and first order resulting into the elimination of bromine atom with rate constant $k = 10^{12.32}\,(s^{-1})\ e^{-190.37\ (kJ/mol)/RT}$.

Kim *et al.* [10], using the conventional static system in the temperature range 380-420 °C, studied the gas phase thermal decomposition of 1-bromo-3-chloropropane in the presence of a radical inhibitor and pressure range of 10-100 Torr. The rate expressions for the elimination reactions of HBr and HCl were found to be,

$k_{(CH2=CH-CH2-Br)} = 10^{13.41}(s^{-1})\ e^{-209.53(kJ/mol)/RT}$ and $k_{(CH2=CH-CH2-Cl)} = 10^{12.43}\ (s^{-1})\ e^{-221.17\ (kJ/mol)/RT}$ respectively.

A recent study of halogenated hydrocarbons is reported by Karin Roy *et al.* [11] They decomposed 2-chloropropene and 2-bromopropene in a single pulse shock tube experiments in the temperature range 1100 to 1250 K and pressure of 150 to 800 kpa. The products under all conditions are propyne and allene with HX elimination.

In the present study, investigation of kinetics of the thermal gas phase decomposition of 1-chlorohexane was carried out, in the temperature range 623 - 833 K, as no study of this kind is available in the literature at lower temperature and especially on static system.

Results and Discussion

The kinetics of the decomposition of 1-chlorohexane was investigated in reaction vessels

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which had been "aged" by the pyrolysis of excess pressure of hexamethyl disiloxane at 750 K for 72 hours. Initial runs were carried out in the unpacked reaction vessel with 10 Torr initial pressure of 1-chlorohexane. Time dependence of the reaction was studied in the unpacked vessel. The reaction was monitored up to 90 minutes at five different temperatures and the rate constants were determined. The value of rate constant for the overall loss of reactant was obtained by monitoring the remaining concentration of the reactant at given time and plotting log [% un-reacted reactant] against time based on following first order rate equation

$$\text{Log } [\%A]_t = \text{Log } [A]_o - k\,t/2.303$$

where

$[\%A]_t$ = % peak area of the remaining reactant at given time t.

$[\%A]_o$ = initial % peak area of reactant

k = first order rate constant s^{-1}

t = time in seconds

A representative first order rate plot for the loss of 1-chlorohexane at 653 K (10 Torr initial pressure) is shown in Fig. 1. The reaction was found to be first order up to 30 % decomposition.

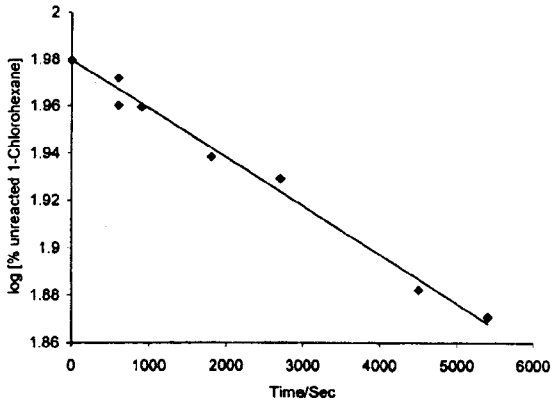

Fig. 1: First order rate plot for the loss of 1-Chlorohexane at 653.16 K. (Initial pressure 10 Torr).

The effect of the surface on the reaction was studied at 653.16 K, using the packed reaction vessel. Kinetic runs were carried out in both reaction vessels with a pressure of 10 Torr and it was found that the reaction proceeded 10 % faster in the packed vessel than the unpacked reaction vessel.

The effect of pressure on the reaction was investigated at 653.16 K. A series of 10 minute pyrolysis with initial pressure in the range of 5 - 20 Torr were made. There was Ca. 10.3 % increase in the rate of reaction as the pressure was lowered from 20 to 5 Torr. It was not obvious whether or not; part or all of this change was due to residual decomposition on the analytical column which as a proportion increased as the amount of material on the column decreased. The behaviour is qualitatively the same as would be observed from competing first and zero order (perhaps surface catalyzed) reactions, but the difference in rates between the packed and unpacked vessels is insufficient to explain the effect quantitatively. Similar results were obtained by Flowers and Honeyman in their study of thermal gas phase decomposition of 2-(1-methyl ethoxy)-propene [12]. Temperature dependence of the rate of overall loss of reactant was studied in the range 623 - 683 K at five different temperatures with an initial pressure of 10 Torr of 1-chlorohexane. Values of rate constants at different temperatures are given in table 1. A linear least square software was used to calculate the Arrhenius activation energy and the exponential factor. The Arrhenius dependence of the rate constant is given by following rate expression

$$k_{(total)} = 10^{9.84\pm 1.08}\, s^{-1} \exp^{-177.25\pm 3.55\ (kJ/mole)/RT}$$

The observed activation energy and frequency factor is consistent with the elimination of hydrochloric acid via four-member cyclic transition state.

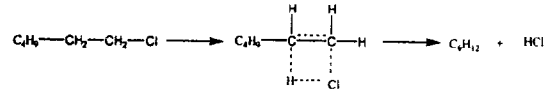

Table-1: Rate constants for the decomposition of 1-chlorohexane at 10 Torr initial pressure in unpacked reaction vessel

Temp/K	$k/10^{-5}\ s^{-1}$
623.2	1.15
643.2	2.30
653.2	4.61
673.2	11.5
683.2	23.0

A comparison of the present results with other similar studies reported in the literature is given in

Table 2. Summary of data on hydrogen halide elimination from some halogenated compounds

Reactants	Products	logA/s^{-1}	Ea/kJmol^{-1}	Ref.
C_2H_5Cl	$HCl + C_2H_4$	13.33	235.3	13
n-C_3H_7Cl	$HCl + CH_3CH=CH_2$	13.44	229.28	14
n-C_3H_7Cl	$HCl + CH_3CH=CH_2$	13.5	230.31	15
n-C_4H_9Cl	$HCl + 1\text{-}C_4H_8$	13.63	231.14	15
n-$C_5H_{11}Cl$	$HCl + 1\text{-}C_5H_{10}$	14.61	243.61	16
n-$C_6H_{13}Cl$	$HCl + 1\text{-}C_6H_{12}$	14.1	236.13	17
$CH_2=CHCH_2Cl$	$HCl + CH_2=C=CH_2$	12.43	221.17	10
tert-C_4H_9Cl	$HCl + iso\text{-}C_4H_8$	13.93	191.23	13
t-$C_4H_9CH_2Cl$	HCl + other products	13.26	251.1	18
Butane, 2-chloro-2,3,3-trimethyl-	$HCl + (CH_3)_3CC(CH_3)=CH_2$	13.8	175.44	19
Heptane, 3-chloro-3-methyl-	HCl + other products	12.38	158.81	20
$C_4H_9\text{-}CH_2\text{-}CH_2\text{-}Cl$	$C_4H_9\text{-}CH=CH_2 + HCl$	9.84	177.25	This work

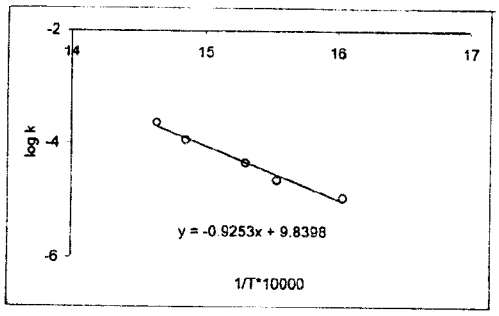

Fig. 2: Arrhenius plot for gas-phase thermal decomposition of 1-chlorohexane.

Table-2. It is obvious that the rate constants derived here are in quite good agreement with the previous work based on *ab-initio* calculations and experimental results. Nevertheless, it is possible that the degree of agreement may partly be due to the compensation of errors in the A-factor and activation energies. This suggests that the effect of halogen substitution in 1, 2 elimination is not affected by the double bond. The effect of methyl substitution is very prominent as the rate constants are very much different from normal alkyl halides. This is contrary to the situation for the chloro-compounds. Vinyl chloride is much more stable and the differences are in fact similar to that for the alkyl chlorides compounds.

Experimental

Material

1-chlorohexane (f.p 26 °C, b.p 132-136 °C) was obtained commercially (Acros, 99+ %) and tested for impurities by Gas Chromatography. Mesitylene (Acros) was used as radical scavenger.

Apparatus

All kinetics experiments were performed using high vacuum pumping system VPC-050 (OSK). Aged Pyrex reaction vessels were used. Two reaction vessels were employed, one packed with short tubing to give a surface to volume ratio (S/V) of Ca. 12 cm^{-1} and the other of similar external dimensions but not packed. The reactions vessels were kept at constant temperature in a salt bath constructed out of stainless steel can, 30 cm in depth, 21 cm in diameter which was logged and terniary eutectic enclosed in 42 x 42 x 44 cm steel box. The salts used were of sodium nitrite (7.1 moles), sodium nitrate (1 mole) and potassium nitrate (6.4 moles). The bath was heated by heater made up of 8 meters length of stainless steel heating cable. A controller of Honeywell company model DC 1010CT-311-000-E, governing the power to the heater, controlled the temperature to ± 1 °C over the temperature rang 275 – 450 °C.

Analyses of the reactants and product samples were carried out on a Shimadzu Model GC 7AG Gas Chromatograph with FID using pre-packed column of (2.1m x 2.6mm) SF-96 % GQ. Typical chromatographic conditions used in this study were: carrier gas = N_2, Flow rate of carrier gas = 45 mL/min, air pressure = 0.5 kg/cm^2, hydrogen pressure = 1.0 kg/cm^2, column temperature = isothermal at room temperature, injection port temperature = 170 °C. The areas under the peaks were determined using spectra physics computing integrator Model SP-4600.

Conclusions

1-chlorohexane decomposes in the temperature range 623 - 833 K and pressure between 5-20 Torr. The decomposition proceeds by a unimolecular mechanism. The homogeneous unimolecular mechanism obeys first order kinetics and the rate constant, which is independent of initial pressure, can be represented by

$$k_{(total)} = 10^{9.84\pm 1.08}\ s^{-1} \exp^{-177.25\pm 3.55\ (kJ/mole)/RT}$$

The pressure dependence study indicates that the Arrhenius parameters obtained in this work are not the high pressure limiting values.

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