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A Gas-Phase Kinetic Study on the Thermal Decomposition of 2-Chloropropene[1]

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Abstract—The gas-phase thermal decomposition of 2-chloropropene in the presence of a radical inhibitor was studied in the temperature range of 668.2–747.2 K and pressure between 11–76 Torr using the conventional static system. The dehydrochlorination to propyne and HCl was the only reaction channel and accounted for >98% of the reaction. The formation of propyne was found to be homogeneous and unimolecular and follows a first-order rate law. The observed rate coefficient is expressed by the following Arrhenius equation:

$$k_{\text{total}} = 10^{13.05 \pm 0.46}\ (\text{s}^{-1})\exp^{-242.6 \pm 6.2\ (\text{kJ/mol})/RT}.$$

The hydrogen halide elimination is believed to proceed through a semipolar four-membered cyclic transition state. The presence of a methyl group on the α-carbon atom lowered the activation energy by 47 kJ mol^{-1}. The experimentally observed pressure dependence of the rate constant is compared with the theoretically predicted values that are obtained by RRKM calculations.

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INTRODUCTION

The dehydrohalogenation reaction of alkyl halides to yield the corresponding olefins has been extensively studied and has been reviewed by Maccoll [1, 2]. The nature of the reaction that occurs upon pyrolysis of an alkyl halide, i.e., whether unimolecular or free radical, homogeneous or heterogeneous, depends upon the halogen involved and upon the structure of the compound concerned. With experiments involving the use of inhibitor and seasoned reaction vessels, it is possible to isolate a unimolecular homogeneous mode of pyrolysis, which is now widely accepted to involve a semi-ionic 4-centered activated complex [3].

Due to the scarcity of data on C_3 vinyl halides and to expand the database, we decided to study the thermal gas-phase decomposition of 2-halopropenes under static conditions using seasoned reactors and in the presence of a radical inhibitor. In earlier paper [4] we reported the thermal decomposition of 2-bromopropene. The mechanism for the gas-phase elimination of hydrogen bromide was described in terms of a semipolar 4-centered activated complex where the replacement of H by CH_3 increased the rate of reaction and lowered the activation energy by 41 kJ mol^{-1}.

In this paper we report gas phase decomposition of 2-chloropropene. The pyrolysis of 2-chloropropene in our conventional static system was carried out in the temperature range of 668–747 K. The dehydrochlorination of 2-chloropropene in the presence of free radical inhibitor *n*-hexane was found to be homogeneous and first order unimolecular. The results are compared with the high temperature single pulse shock tube study [5].

The pressure dependence of the rate constants was also studied. The Rice–Ramsperger–Kassel–Marcus (RRKM) unimolecular theory was compared with experimental data for the pressure dependence.

EXPERIMENTAL

Materials

2-Chloropropene (F.p, –34°C, bp 22.5–22.8°C) was obtained commercially (ACROS, 98%) and tested for impurities by gas chromatography. *n*-Hexane (Merck) was used as the radical inhibitor.

Kinetic Experiments

Kinetic studies were carried out as detailed in our earlier communication [4] in a conventional static vacuum system with two Pyrex reaction vessels. One of the reaction vessels was packed with short lengths of pyrex tubing to give a surface-to-volume ratio $S/V = 12$ cm^{-1}; the other was of similar external diameter but not packed. The reaction vessels were aged prior to kinetic runs by pyrolysis of excess amounts of 2-chloropropene at 750 K for 72 h. Greaseless stopcocks (Rotaflo) were specifically used in all those parts of the vacuum line that were in contact with the pyrolyzed materials.

[1] This article was submitted by the authors in English.

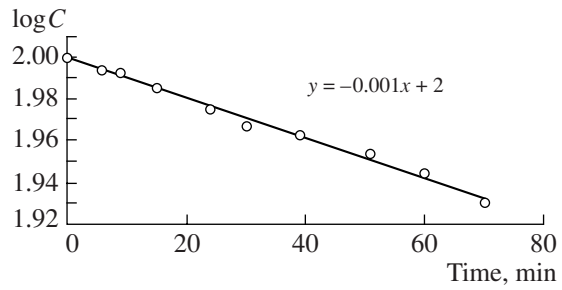


Fig. 1. First order rate plot for the loss of 2-chloropropene at 727.2 K.

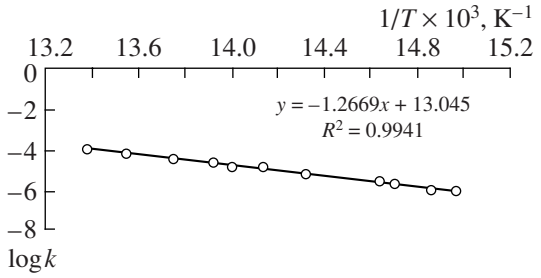


Fig. 2. Arrhenius plot for thermal decomposition of 2-chloropropene for the inhibited reaction.

Reaction vessels were immersed in a fused salt ($NaNO_3/NaNO_2/KNO_3$ ternary eutectic) thermostat, the temperature of which was maintained to ±1 K by a Honeywell DC 1010 temperature controller. Temperature was measured with a *K*-type thermocouple. The pressure in the reactor was reduced to about 10^{-3} mm of Hg by a VPC-050 (OSK) high vacuum pumping system. A uniform period of 20 min of evacuation before each run was adopted. This is very necessary because, if the reactor is not properly evacuated, the succeeding run is slower than usual and the reproducibility of results becomes very unsatisfactory.

Analyses were carried out by gas chromatography using a Shimadzu GC-7AG gas chromatograph fitted with a $6' \times 1/16''$ prepacked Porapak Q column. A flame ionization detector coupled to a spectra physics Model SP-4600 data jet integrator was used for quantitative determination of the eluted compounds. Typical chromatographic conditions were used in the present study: column oven temperature = 70–170°C, temperature programming rate = 32 K/min, carrier gas = N_2, flow rate of carrier gas = 60 ml/min, hydrogen pressure = 1 kg/cm², air pressure = 0.5 kg/cm², injection port temperature = 170°C. The identification of the reaction products was confirmed from comparison of retention time with those of standards.

Table 1. Rate constants for 2-chloropropene decomposition at 12 Torr initial pressure

Temperature, K	$k \times 10^5$, s^{-1}
668	0.13
673	0.14
680	0.26
683	0.38
698	0.77
707	1.60
714	1.79
718	2.80
727	3.84
738	7.20
747	12.80

RESULTS AND DISCUSSION

The gas phase elimination kinetics of 2-chloropropene to propyne was determined between the temperature range of 668.2–747.2 K and pressure range of 11–76 Torr. This elimination, in the seasoned reaction vessel and the presence of 1% of the radical inhibitor *n*-hexane, is homogeneous and unimolecular and follows a first order rate law.

$$CH_2{=}C(Cl){-}CH_3 \longrightarrow CH{\equiv}C{-}CH_3 + HCl.$$

First order rate plots for the loss of 2-chloropropene using 12 Torr initial pressure were linear as shown in Fig. 1. The rate constants based on the loss of initial reactant were obtained at eleven temperatures and are listed in Table 1. The Arrhenius parameters were calculated from the plot of $\log k$ versus $1/T$ (Fig. 2), and the rate constant expression based on these parameters is given below:

$$k_{total} = 10^{13.05 \pm 0.46}\ (s^{-1}) \exp^{-242.6 \pm 6.2\ (kJ/mol)/RT}.$$

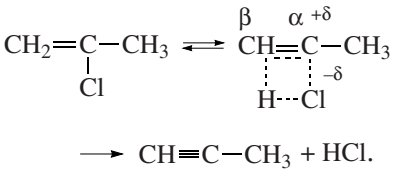
The homogeneity of the reaction was checked, under the free radical inhibitor *n*-hexane, by using a packed reaction vessel with a surface-to-volume ratio 12 times greater than the unpacked reaction vessel. In the packed reaction vessel, the rate of reaction of 2-chloropropene gave results identical to those that had been obtained in the unpacked vessel.

The effect of pressure on the rate of formation of propyne was investigated at 727.2 K and pressure between 11–76 Torr. The data is represented in Fig. 3 in the form of percent propyne versus pressure. It can be seen that no significant trend is observed with changes in pressure, and it can be concluded that true unimolecular rate expressions are being determined.

Table 2. High pressure arrhenius parameters for decomposition of alkyl chloride

Reactant	E_a, kJ mol^{-1}	log$A$, s^{-1}	log$k$ at 600 K	Ref.
C_2H_3Cl	290	14	–11.24	[6]
2-C_3H_5Cl	242.6 ± 6.2	13.05	–8.06	This work
C_2H_5Cl	228 ± 8	14.03	–6.30	[7]
2-C_3H_7Cl	213	13.55	–4.99	[8]

The observed Arrhenius parameters, log$A$ = 13.05 s^{-1} and E_a = 242.6 kJ mol^{-1}, are consistent with the semi-ionic four-centered transition state for the elimination of HCl.



Comparison of the rate constants of 2-chloropropene with vinyl chloride at 600 K shows that the former reaction is three orders of magnitude faster (see Table 2). Assuming a similar transition state in both reactions, this increase in rate can be assigned entirely to a change in activation energy. The observed reduction of 47 kJ mol^{-1} for 2-chloropropene compared to vinyl chloride can be attributed to the stabilization of the transition state due to the presence of a methyl group at the α-carbon atom.

To find whether the rate constant given above has any pressure dependence, Rice, Ramsperger, Kassel, and Marcus (RRKM) theory calculations were carried out. The input parameters for RRKM calculations are summarized in Table 3. Vibrational frequencies of the 2-C_3H_5Cl molecule and those of its complex were obtained from the results of Bae et al. [9]. The moment of inertia was calculated from the geometries of 2-C_3H_5Cl models of the molecule and activated complex at the B3LYP level in reference [9]. The $\Delta_f H°$ of the 2-C_3H_5Cl molecule was obtained from the NIST Kinetics Database [10], and that of its complex was assumed to have a value that gave a similar Arrhenius A-factor to the experimental results. Other adjustable parameters were altered accordingly. The activation energies and A-factors for the experimental and RRKM treated data are found to be 242.6 and 242.21 kJ mol^{-1} and 13.05 and 13.04 s^{-1}, respectively (Fig. 4). This is in agreement with the conclusion of Benson and Bose [11] that the critical energies for the alkyl halide elimination reactions are between 209.2 and 251.04 kJ mol^{-1}. The actual difference between both the experimental and the calculated results is 0.35 kJ mol^{-1} and 0.01 s^{-1} in activation energy and A-factor, respectively, which is negligibly small and is within the combined experimental errors of all determinations.

The fall-off behavior was interpreted by performing RRKM calculations using the same software program "ChemRate." The pressure dependent rate constants were calculated at a collision efficiency of 0.2. The comparison of the RRKM calculated and experimental

Table 3. Input parameters used in RRKM calculation for 2-chloropropene decomposition

Species	Frequencies, cm^{-1}	Moment of inertia, $\times 10^{55}$, kg^3 m^6	Heat of formation, kJ/mol
2-C_3H_5Cl	3248, 3115, 3156, 3032, 1699, 1490, 1435, 1412, 1193, 1021, 930, 629, 403, 348, 3087, 1471, 1073, 918, 451, 712, 210	1.8643	–24.7*
2-$C_3H_5Cl^{\#}$	3264, 3151, 3147, 3005, 1512, 1478, 1376, 1347, 1247, 1006, 943, 711, 397, 373, 3044, 1428, 1020, 941, 466, 329	1.7069	214**

* Ref. [10].
** Adjusted to get best fit.

Table 4. Comparison of Arrhenius parameters determined by various methods for thermal decomposition of 2-chloropropene

Method	T, K	E_a, kJ mol^{-1}	log$A$, s^{-1}	r*	Ref.
Shock tube (at 100 Torr)	1127–1221	268.89	14.05	0.9959	[5]
Static system	668–747	242.56	13.05	0.9970	This work
RRKM	838–997	242.47	13.06	1	This work

* r, Correlation coefficient of Arrhenius plots.

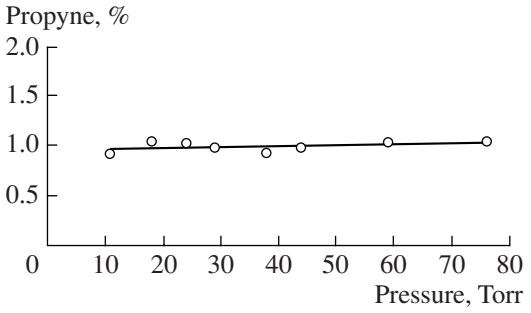


Fig. 3. Pressure dependence study for the decomposition of 2-chloropropene at 727 K (reaction time 5 min).

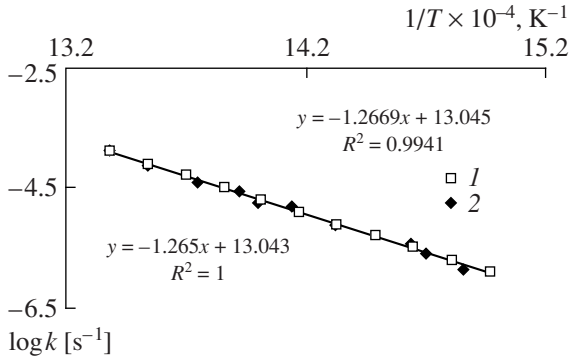


Fig. 4. Comparison of theoretical and experimental rate constants for thermal decomposition of 2-chloropropene. Filled diamonds are for experimental results, and empty squares denote theoretical data.

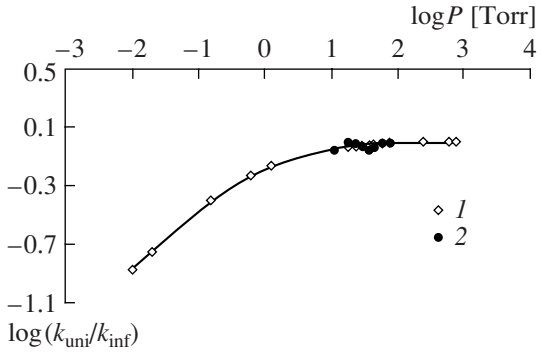


Fig. 5. Comparisons of calculated and experimental fall-off curves for 2-chloropropene at 727.2 K. Filled circles represent experimental results, and open diamonds are for theoretical data.

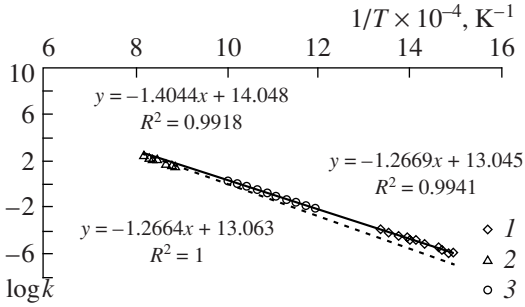


Fig. 6. Arrhenius plot showing (*1*) comparison of static, (*2*) shock tube [5], and (*3*) RRKM treated data for thermal decomposition of 2-chloropropene. Triangles denote shock tube results, circles are for RRKM treated data, and diamonds are for static system investigations.

fall-off curves at the collision efficiency of 0.2 is represented in Fig. 5. It can be seen that the Arrhenius parameters obtained in this work are high pressure limiting values.

RRKM calculations were also carried out in the temperature range 838–997 K. The rate constants thus obtained were plotted in combination with shock tube [5] (at 100 Torr) and present static system investigations. There is a linear relationship between these three results (Fig. 6). Comparisons of Arrhenius parameters determined by these methods are given in Table 4. From the comparison of these two studies, it can be found that the present study supports the results of the earlier shock tube study [5]. The rate parameters derived from this study and the earlier shock tube study are in good agreement. It can be seen that the discrepancies are within the error limits. However, a quantitative comparison of the differences in the Arrhenius parameters for the two sets of experiments shows that the present results differ by 6.3 and 7.12% in activation energy and *A*-factor, respectively. This is acceptable and may be attributed to small cumulative errors in calibration and sample preparation.

CONCLUSIONS

The thermal decomposition of 2-chloropropene has been studied in the temperature range of 662.2–747.2 K and pressure between 11–76 Torr in a static reactor. The reaction is homogeneous and unimolecular, and the rate expression for the inhibited reaction is found to be

$$k_{\text{total}}\,(\text{inhibited}) = 10^{13.05 \pm 0.46}\,(\text{s}^{-1})\exp^{-242.6 \pm 6.2\ (\text{kJ/mol})/RT}.$$

The pressure dependence study and RRKM calculations show that the Arrhenius parameters obtained in this work are high pressure limiting values. The ChemRate calculated rate constants exactly coincided with the experimental data. The rate parameters derived from this study and earlier shock tube studies are in good agreement within the combined experimental errors of all determinations.

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