ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 4, pp. 487–492. © Pleiades Publishing, Ltd., 2011.
Published in Russian in Kinetika i Kataliz, 2011, Vol. 52, No. 4, pp. 498–503.

Kinetics of the Gas-Phase Thermal Decomposition of 3-Bromopropene

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Received November 30, 2010

Abstract—The thermal decomposition of 3-bromopropene was investigated in the temperature range 568.2–653.2 K and pressures between 14–64 Torr in static Pyrex reaction vessel. The reaction was shown to be homogeneous gas reaction of the first order with more than 60% conversion. For the overall reaction, E_a = 153.67 ± 6.70 kJ mol^{-1}, and log$A$ (A, s^{-1}) = 9.46 ± 0.57. Two mechanisms, dehydrohalogenation molecular elimination and C–Br bond fission are discussed, both of which account for the observed kinetics and products of decomposition. To interpret the fall-off behaviour, RRKM/ME calculations were adopted and the pressure dependent rate constants were calculated at collision efficiency of 0.25. From the pressure dependence study and RRKM calculations, it can be deduced that we are at the high-pressure limit.

Keywords: Kinetics study, 3-bromopropene, static system, unimolecular reaction, pyrolysis gas-chromatography, thermal degradation.

DOI: 10.1134/S0023158411040100

1. INTRODUCTION

There is one previous study of dehydrohalogenation reaction of 3-bromopropene using static system by Kim et al., [1]. Actually their study was on the thermal decomposition of Br–CH_2–CH_2–CH_2–Cl. They determined the total molecular dissociation rate constant, for the decomposition of Br–CH_2–CH_2–CH_2–Cl in the temperature range 653–693 K and in the pressure range of 10–100 Torr. They derived reported rate expression for 3-bromopropene and 3-chloropropene by fitting to a complex mechanism. That means there is no direct study of the 3-bromopropene in a static system and our results are first of the kind. As per the assertion of Kim et al., since C–Br bond fission to give Br is expected to have much higher activation energy, the disappearance of original compound is reasonably assumed to occur via low energy HBr elimination step. However, we are of the view that the possibility of unimolecular decomposition of 3-bromopropene into allene and HBr though exist, could not be favoured over C–Br bond fission due to high value of dissociation energy for C–H or C–C bonds. Hence, contrary to the assertion of Kim et al., we expect that along with the dehydrohalogenation molecular elimination, the thermal decomposition of 3-bromopropene would also result in rupturing of the weakest C–Br bond with the formation of an allyl radical and bromine atom.

In order to determine the high-pressure limiting Arrhenius parameters as well as the pressure-dependence of the rate constants, we have utilized the ChemRate software package [2] to perform RRKM/Master Equation (RRKM/ME) calculations.

2. EXPERIMENTAL

2.1. Materials

3-bromopropene (Fp. –2°C, bp 70–71°C) was obtained commercially (ACROS, 98%) and tested for impurities by Gas Chromatography. Mesitylene (ACROS), *n*-hexane and toluene (Merck) were used as radical inhibitors.

2.2. Kinetic Experiments

Kinetic studies were carried out as previously described [3–6] 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) of ca. 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 amount of 3-bromopropene at 730 K for 48 h. Rotaflo Teflon greaseless stopcocks

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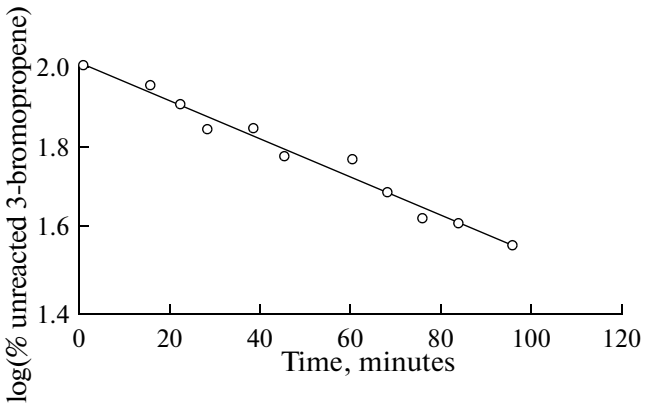


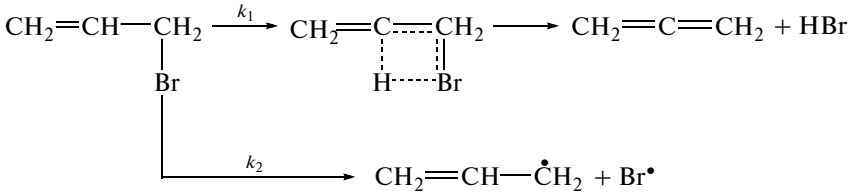
Fig. 1. First order rate plot for the loss of 3-bromopropene at 603.2 K.

were specifically used in all those parts of the vacuum line, which were in contact with the pyrolyzed materials. 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°C by 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 VPC-050 (OSK) high vacuum pumping system. For reproducible results a uniform period of 20 min of evacuation before each run was adopted.

Analyses were carried out by Gas Chromatography using a Shimadzu GC-7AG gas chromatograph fitted with 6' × 1/16" pre-packed Porapak Q column. A flame ionization detector coupled to spectra physics Model SP-4600 data jet integrator was used for quantitative determination of the eluted compounds. Typical chromatographic conditions used in the present study: Column oven temperature = 70–170°C, Temperature programming rate = 32°C/min, Carrier gas = N_2, Flow rate of carrier gas = 23 mL/min, Hydrogen pressure = 1 kg/cm^2, Air pressure = 0.5 kg/cm^2, Injection port temperature = 170°C. The identification of the reaction products was confirmed from comparison of retention time with those of standards.

3. RESULTS AND DISCUSSION

Thermal decomposition of 3-bromopropene was studied in the temperature range 568.2–653.2 K with an initial reactant pressure of 20 Torr. Allene and 1,5-hexadiene are the only products formed. These products are formed via two competing homogeneous mechanisms. First of these, the retro-ene molecular elimination reaction to form allene and hydrogen bromide. The second is the C–Br bond fission to give allyl radical, which accounts for 80% of the 3-bromopropene decomposed at highest temperature. The reaction scheme for the decomposition of 3-bromopropene is presented below:



Reaction Scheme.

First order rate plots for the total loss of 3-bromopropene using 20 Torr initial pressure were linear. A representative plot is shown in Fig. 1. The rate constants for the molecular elimination channel were obtained from the plots of % yield of allene against % conversion based on following rate law

$$[\%\text{Allene}]_t = [\%\text{Allene}]_0 + k_1/k_{(\text{total})}[(3\text{-Bromopropene})_0 - (3\text{-Bromopropene})_t].$$

From the slopes of these plots the values of rate constants for the formation of allene (k_1) were calculated as

$$\text{slope} = k_1/k_{(\text{total})}$$
$$k_1 = k_{(\text{total})} \times \text{slope}.$$

The rate constants for C–Br bond fission channel leading to allyl radical formation was calculated as

$$k_{(\text{total})} = k_1 + k_2,$$
$$k_2 = k_{(\text{total})} - k_1.$$

The values of $k_{(\text{total})}$, k_1 and k_2 obtained at various temperatures are given in Table 1. From the temperature dependence of rate constant, activation energy (E_a) and the frequency factor (A) for each reaction were obtained using Arrhenius expression. The Arrhenius parameters were determined from the plot of log$k$ Vs. $1/T$ (Fig. 2).

$$\log k = \log A - E_a/2.303RT.$$

Table 1. First order rate constant for the decomposition of 3-bromopropene

Temperature, K	$k_{(total)}/10^{-4}$ s^{-1}	$k_1/10^{-5}$ s^{-1}	$k_2/10^{-5}$ s^{-1}
568.2	0.24	0.462	1.94
574.2	0.288	0.666	2.21
581.2	0.366	0.772	2.90
592.2	0.768	1.74	5.94
603.2	1.82	3.49	14.70
615.2	3.99	8.86	31.00
627.2	5.12	13.20	38.00
638.2	7.68	24.20	52.60
646.2	10.20	36.10	65.90
653.2	13.00	50.70	79.30

A linear least square program was used to obtain the E_a and A values with statistical 95% certainty limits. In the Arrhenius form rate constants are expressed as follows

$$k_{(total)} = 10^{9.46 \pm 0.57}(s^{-1})\exp^{-153.67 \pm 6.7\ (kJ/mol)/RT},$$
$$k_1 = 10^{10.70 \pm 0.35}(s^{-1})\exp^{-175 \pm 4.1\ (kJ/mol)/RT},$$
$$k_2 = 10^{8.61 \pm 0.71}(s^{-1})\exp^{-145.2 \pm 8.2\ (kJ/mol)/RT}.$$

The representative Arrhenius plots for the overall loss of the reactant and the formation of allene and fragmentation products are shown in Figs. 2, 3 and 4 respectively.

The effect of surface on the reaction was investigated using the packed reaction vessel with a surface to volume ratio of ca. 12 cm^{-1} at 20 Torr initial reactant pressure. We observed, however, no increase in the rate of decomposition in the packed reaction vessel.

Similarly no retarding effect was observed on the decomposition of 3-bromopropene, when experiments were carried out in the presence of different amount of *n*-hexane, mesitylene and toluene. This shows the homogenous nature of the reaction.

The first order of the reaction was also demonstrated by varying the pressure of 3-bromopropene in the range 14–64 Torr at 603.2 K. Table 2 contains the results obtained for various pressures of allyl bromide for 30 minutes pyrolysis time. The pressure depen-

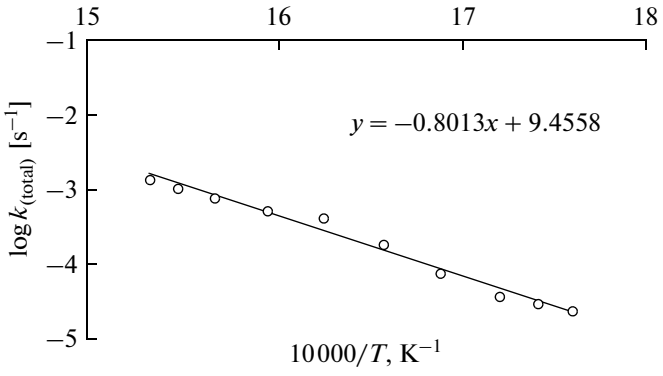


Fig. 2. Arrhenius plot for the total decomposition of 3-bromopropene.

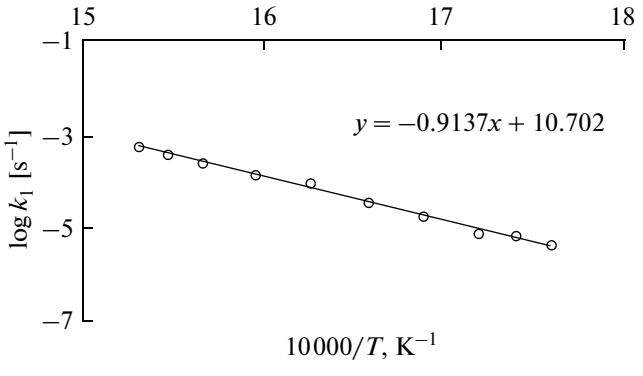


Fig. 3. Arrhenius plot for the formation of allene as molecular elimination product.

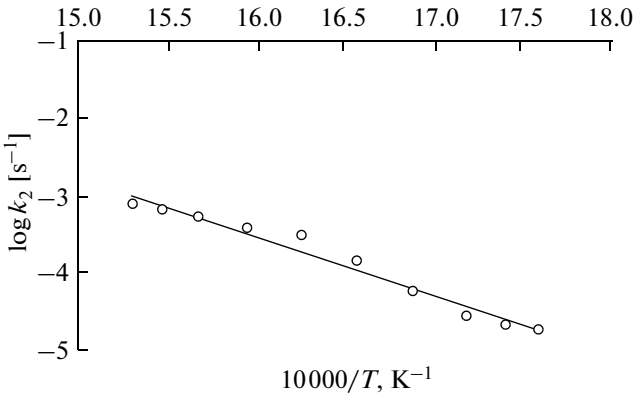


Fig. 4. Arrhenius plot for the formation of products from C–Br fission.

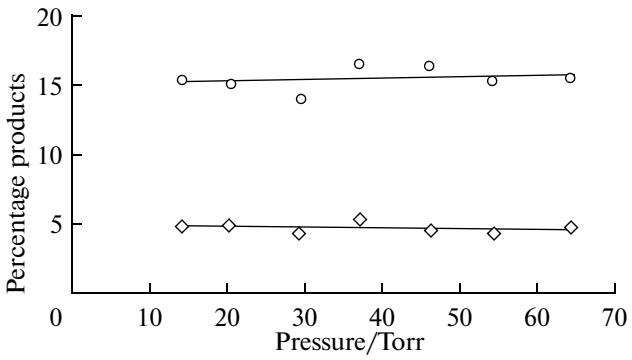


Fig. 5. Pressure dependence of products from the pyrolysis of 3-bromopropene at 603.2 K (pyrolysis time 30 minutes). Diamonds represent allene and squares denote 1,5-hexadiene.

dence of the products from the thermal decomposition of 3-bromopropene is represented in Fig. 5 in the form of percent product versus pressure. As can be seen from the figure, the results show no significant trend with changes in pressure and it can be concluded that first order rate expressions are being determined.

The formation of allene at lower temperature and lower conversion shows a clean unimolecular decomposition of 3-bromopropene resulting into the formation of a single peak of allene with elimination of HBr. However, at high conversion the appearance of another product opens the question as to which of the two possible mechanism of decomposition operates in the case of 3-bromopropene. The two possible mode of decomposition are dehydrohalogenation molecular elimination (mechanism 1) and C–Br bond fission (mechanism 2).

Table 2. Pressure dependence of the first order rate constant for overall decomposition of 3-bromopropene at 603.2 K for 30 minutes kinetic runs

Pressure/Torr	$k_{(total)}/10^{-4}$ s^{-1}
14	1.25
20	1.24
29	1.12
37	1.37
46	1.31
54	1.21
64	1.25

The mechanism (1) is a clean unimolecular decomposition where as the mechanism (2) operates as a result of C–Br bond fission. Now it is quite clear that at lower conversion, mechanism (1) is operative where as at high conversion the contribution of C–Br bond fission is more dominant and becomes increasingly important. The major reaction is C–Br bond fission to form allyl radicals. These radicals are fairly stable due to the resonance stabilization [7, 8] and the only possibility is their recombination to give 1,5-hexadiene and this is consistent with most of the earlier studies [9–11]. Also there is no possibility of allene formation from allyl radicals because of the relatively high value of dissociation energy for C–H bond. This is in accord with the observations of Szwarc et al. [9, 12] and Sehon et al. [13]. That means the observed allene is coming from molecular elimination reaction which is a minor pathway corresponding to (~30%) of the 3-bromopropene reacted, the rest 70% decompose via C–Br bond fission. All we can say for allyl radicals is that, it is recombining to give 1,5-hexadiene as

$$^{\bullet}C_3H_5 + {}^{\bullet}C_3H_5 \longrightarrow C_6H_{10}.$$

Our reaction scheme showing two pathways for 3-bromopropene is most promising; as we have no experimental evidence to show that allyl radical is participating in any chain propagation. Our basic important results i.e. the rate expressions for $k_{(total)}$, k_1 and k_2 provide sufficient information based on our experiment.

To ascertain whether the rate constants determined experimentally have any pressure dependence, RRKM calculations [14, 15] were adopted. In Table 3, the input data for RRKM calculations are given. Vibrational frequencies and moment of inertia of allyl

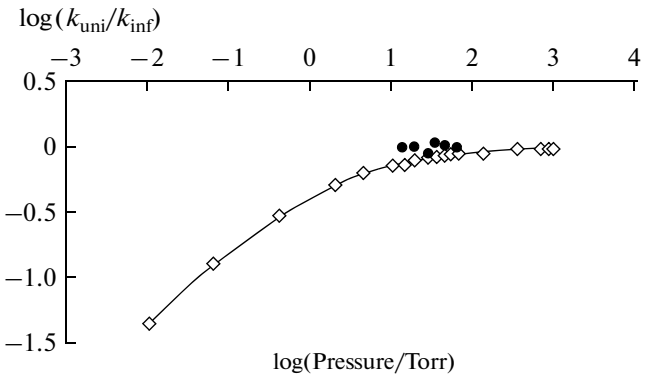


Fig. 6. Comparison of calculated and experimental fall-off curves for 3-bromoropropene at 603.2 K. Filled circles represent experimental results and open diamonds are for theoretical data.

bromide molecule and complex were obtained from the results of Kim et al. [1]. $\Delta_f H°$ of 3-C_3H_5Br was obtained from NIST kinetic data base [16]. Others parameters were adjusted accordingly. Rate constants were determined in the temperature range 568.2–653.2 K. To interpret the fall-off behaviour, RRKM calculations were carried out and the pressure dependent rate constants were calculated at collision efficiency of 0.25. Figure 6 shows the comparison of RRKM calculated and experimental fall-off curve at collision efficiency (β) of 0.25. From the pressure dependence study and RRKM calculations, it can be deduced that we are at the high-pressure limit.

4. CONCLUSIONS

The experimental facts reported in this paper lead to the final conclusion that two possible mechanisms operate in the case of 3-bromopropene. First unimolecular mechanism, with the elimination of HBr and second C–Br bond fission resulting into the formation of Br atom and allyl radical. The allyl radicals recombine together to give 1,5-hexadiene. Taking into account all the arguments mentioned in the discussion we are inclined to assume that mechanism (2) is the most probable reaction. On that basis we suggest 153.6 kJ/mol as the most suitable value for the overall decomposition of 3-bromopropene.

Table 3. Input parameters for *RRKM* calculations for models of molecule and activated complex (3-bromopropene)

Species	Frequencies[a], cm^{-1}	Moment of inertia/10^{-135} kg^3m^6	$\Delta_f H$ 298 K, $kJmol^{-1}$
3-C_3H_5Br	3050(3), 2950(2), 2640, 2440(2), 1415, 1370, 1207, 1172, 1050, 990, 930, 911, 580(2), 417, 290, 200	9.20[b]	47.7[c]
3-$C_3H_5Br^{\#}$	3050(2), 2950(2), 1640, 1440(2), 1310, 1300(2), 990, 970, 910, 850(2), 580(2), 440(2), 223	6.24[b]	243[d]

Note: [a]Number in parentheses signifies degeneracy; [b]Reference [1]; [c]Reference [16]; [d]Adjusted to get best fit; [#]Activated complex.

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