The Thermal Gas-phase Decomposition of Vinyl Bromide

Ko SAITO,* Teiji YOKUBO, Tohru FUSE, Hiroyuki TAHARA, Osamu KONDO,
Tetsuo HIGASHIHARA, and Ichiro MURAKAMI
Department of Chemistry, Faculty of Science, Hiroshima University, Higashi Senda-machi, Hiroshima 730

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The thermal gas-phase decomposition of vinyl bromide in Ar has been studied behind reflected shock waves over the temperature range between 1300 and 2000 K and the density range of $5.2\times10^{-6}-3.8\times10^{-5}$ mol cm^{-3} by monitoring the UV absorption of C_2H_3Br and the IR emission of HBr. The decomposition proceeds *via* the molecular elimination of HBr, and the unimolecular process is in the low-pressure region under the present experimental conditions. The low-pressure-limit rate constant was obtained as

$$k_{2nd} = 10^{13.98\pm0.21}\exp\{-(41.5\pm1.6\ \text{kcal mol}^{-1})/RT\}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The collision efficiency factor, β_c, was obtained as about 2×10^{-4}, considerably lower than that of vinyl chloride.

The thermal decomposition of vinyl fluoride was investigated in a single-pulse shock tube over the temperature range of 1174—1353 K.[1)] The reaction proceeded *via* HF elimination, and the unimolecular process was in the high-pressure region in the total density range of $(3.7-4.8)\times10^{-5}$ mol cm^{-3}. The decomposition of vinyl chloride was measured by means of a time-resolved UV absorption method behind reflected shock waves over the range of 1350—1900 K.[2)] The reaction proceeded *via* HCl elimination and was in the fall-off region in the density range between 7×10^{-7} and 1.6×10^{-3} mol cm^{-3}.

In the case of vinyl bromide, the following two channels are probable for the initiation reaction:

$$C_2H_3Br(+M) \longrightarrow C_2H_2 + HBr(+M) \qquad \Delta H^\circ_{r298} = 26.5\ \text{kcal mol}^{-1} \qquad (1)$$

$$C_2H_3Br(+M) \longrightarrow C_2H_3 + Br(+M) \qquad \Delta H^\circ_{r298} = 76.7\ \text{kcal mol}^{-1}. \qquad (2)$$

From the large difference in the heat of reaction, Reaction 1 seems preferable for the initiation reaction, although its preexponential factor is relatively small because of the four-center reaction. An estimation based on the semiempirical method of Benson and Haugen[3)] suggests that the HBr elimination is much faster than the C–Br bond fission. However, it is not certain whether or not all alkenyl halides decompose *via* molecular elimination, since the difference in the heat of reaction between the two channels becomes small as the halogen changes from F to Br. Thus, at high temperatures, the simple bond fission becomes important as the initiation reaction.

In this work, we measured the concentration profiles of the reactant and HBr produced in order to determine the overall decomposition rate of C_2H_3Br and the production rate of HBr.

Experimental

The experiments were performed in a shock tube made of stainless steel (SUS-304). The test section was 4.52 m long and 9.4 cm in inner diameter, and it was evacuated to less than 5×10^{-6} Torr (1 Torr = 133.322 Pa) by means of a 6-inch oil-diffusion pump. The leak and outgassing rate of this section in the stage just before the run was about 2×10^{-7} Torr l/s. The driver section (1.8 m long and 8.5 cm in inner diameter) was evacuated to about 1×10^{-2} Torr. Hydrogen was used as the driver gas at pressures of 2—6 atm (1 atm = 101325 Pa). Tetoron sheets of 100, 75, 50, and 25 μm were used as diaphragms to separate the two sections. Shock waves were generated by bursting the diaphragm with a needle driven by a solenoid.

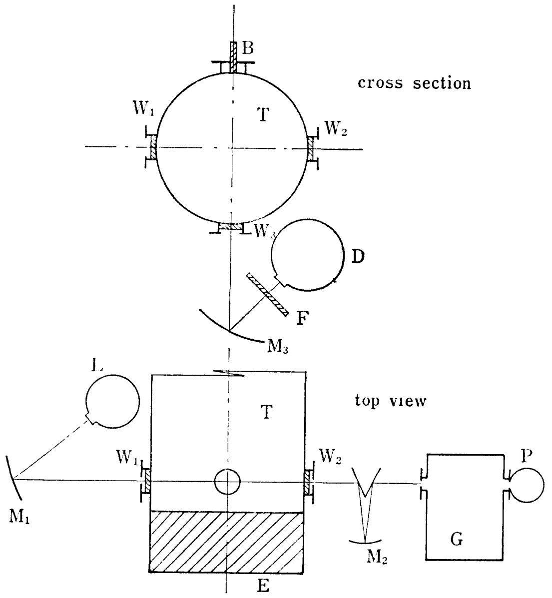

Fig. 1. Experimental arrangement. T: Shock tube, E: end plate, B: pressure gauge, L: deuterium lamp, G: grating monochromator, P: photomultiplier, M_1—M_3: concave mirrors, F: filter, D: InSb detector, W_1: quartz window, W_2 and W_3: CaF_2 windows.

At a distance of 4.44 m from the diaphragm, two sets of windows were mounted in the tube in order to observe the physical properties of the shocked gas. Figure 1 shows the experimental arragement for the absorption and emission experiments. Light from a deuterium lamp (HTV, L544) was focussed on the center of the tube through an inlet slit (4 mm wide and 8 mm high), and the light from an outlet slit (2 mm wide and 8 mm high) was focussed again on the entrance slit (1 mm wide) of a monochromator (Jarrell-Ash, 0.25 M). The average width of the light beam in the tube was 3 mm, while the hight was 8 mm. The light passed through the exit slit (1 mm wide) of the monochromator was detected by a photomultiplier (HTV, R106UH) supplied with a voltage of −800 V. The output signal was fed into a pre-amplifier (IWATSU, DA-2A) and then to a wave-memory (Kawasaki Electronica, M-50E), which was connected to an oscilloscope and a pen-recorder. The response time of the optical-electrical system was less than 10 μs enough for the present study. The IR emission was detected by an InSb photo-voltaic element (HTV, P839A) at 77 K through a filter of 3.9±0.05 μm. The signal-recording system was the same as in the absorption experiment. The response time of this system was about 10 μs. Measurements of the incident shock velocity were performed by counting the time intervals of shock-arrival signals between two pressure gauges mounted on the walls, 32 cm apart from each other, with a universal counter (Takeda Riken, TR-5104G) having an accuracy of 0.1 μs. The attenuation in the shock velocities was estimated to be less than 1% per meter of travel. The measured incident shock velocities were then used to compute the non-reaction conditions behind the reflected shock.

Liquid C_2H_3Br (99.5% stated minimum purity) was purified by trap-to-trap distillations. Ar (99.998%) was used as the diluent, without any further purification. Several mixture (0.03—3.0 mol% C_2H_3Br in Ar) were prepared in a 30-l glass flask. They were allowed to stand for more than 12 h before use.

Results

The experiments were performed behind reflected shock waves over the temperature range between 1300 and 2000 K and the density range of 5.2×10^{-6}—3.8×10^{-5} mol cm^{-3}. Vinyl bromide has an absorption spectrum in the vacuum ultraviolet region with a maximum at 52200 cm^{-1}.[4] At the high temperatures available in shock waves, the absorption may be detected at higher wavelengths. In this work, the absorption experiment was performed at 250 nm with FWHM= 1.7 nm. The absorption coefficient at this wavelength was in the range of $(1—2)\times10^5$ cm^2 mol^{-1} over the temperature range studied, and Lambert-Beer's law was ascertained to hold. Figure 2 shows typical UV absorption (a) and IR emission (b) profiles obtained simultaneously in one experimental run. The absorption profile clearly reveals a decay of the reactant with the time, and the emission profile shows an increase of a product immediately behind the reflected shock front. The polyacetylenes which may be produced in the later part of the reaction have an absorption at this wavelength.[5] However, it is likely that at low temperatures the decay curve does not involve the absorption of products. At high temperatures the effect of the products was seen as a very slow increase in the absorption after a large consumption of the reactant. The decay rate of the reactant was first-order in $[C_2H_3Br]$ up to at least 25% decrease in the reactant. Thus, the first-order rate constant, k_{1st}, was obtained by means of this definition: $k_{1st}=-d(\ln D)/dt$, where $D=[C_2H_3Br]\times\varepsilon\times L$, ε=absorption coefficient, and L= inner diameter of the shock tube. Figure 3 shows an Arrhenius plot of k_{1st} for four different total densities. It appears that the first-order rate constant depends on the total density and that the data corresponding to each constant density are parallel to, but apart from, each other because of the density change. Thus, the apparent decomposition rate is expressed as

$$-d[C_2H_3Br]/dt = k_{2nd}[C_2H_3Br][M].$$

Figure 4 shows an Arrhenius plot of the second-order rate constant, k_{2nd}. The best-fitting line gives an Arrhenius expression as

$$k_{2nd}=10^{13.98\pm0.21}\exp\{-(41.5\pm1.6\text{ kcal mol}^{-1})/RT\}\ \text{cm}^3\text{ mol}^{-1}\text{ s}^{-1},$$

where the error limits denote the standard deviations.

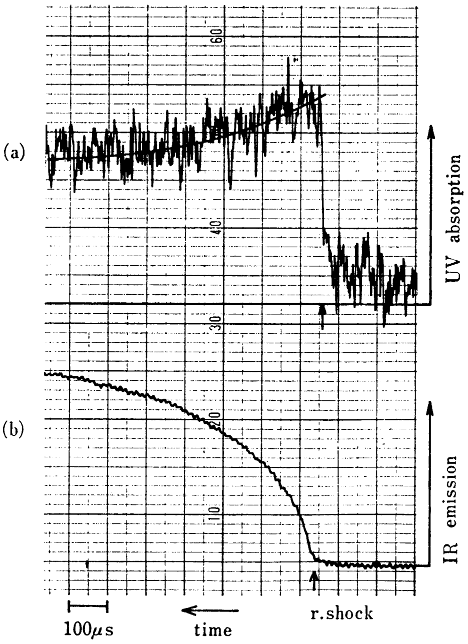

Fig. 2. Typical absorption and emission record in the same experimental run. 1.5 mol % C_2H_3Br in Ar, Temperature=1430 K, Pressure=2.10 atm, $k_{1st}=7.78\times10^2$ s^{-1}, $k_{ir}=2.75\times10^3$ s^{-1}.

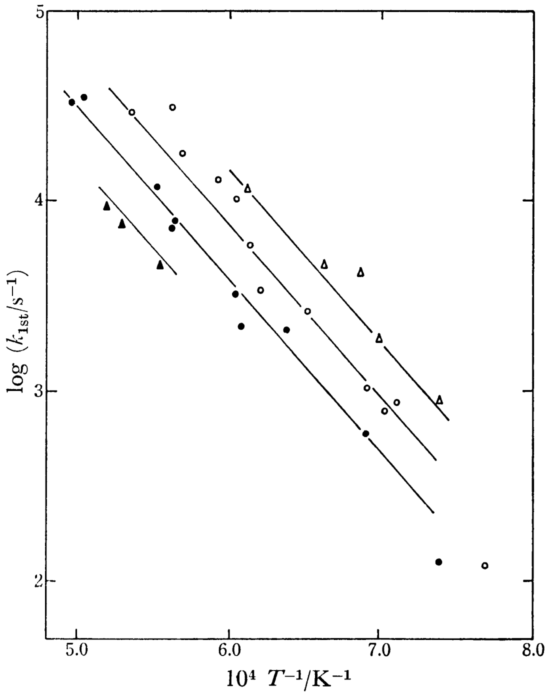

Fig. 3. Arrhenius plot of the first order rate constant k_{1st}. Total density (mol cm^{-3}): ▲=5.2×10^{-6}, ●=1.0×10^{-5}, ○=1.9×10^{-5}, △=3.6×10^{-5}. Straight lines denote the precise change of k_{1st} with the density (relative) assuming that k_{1st} is proportional to the total density.

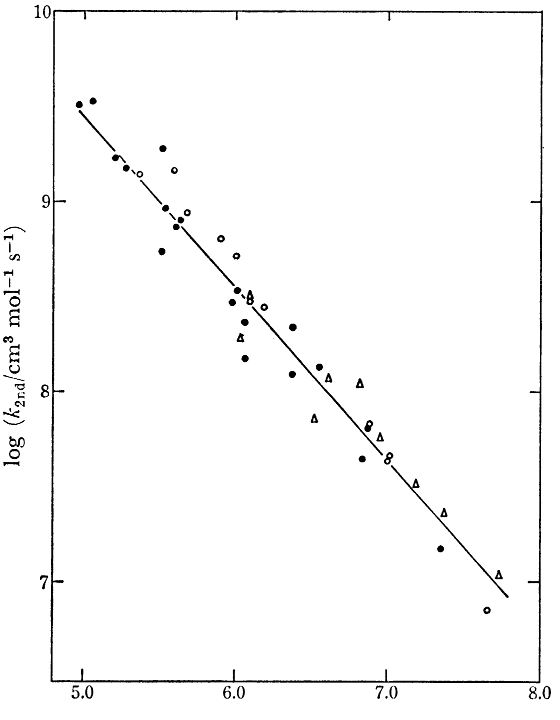

Fig. 4. Arrhenius plot of the second order rate constant. Straight line is the least square evaluation.

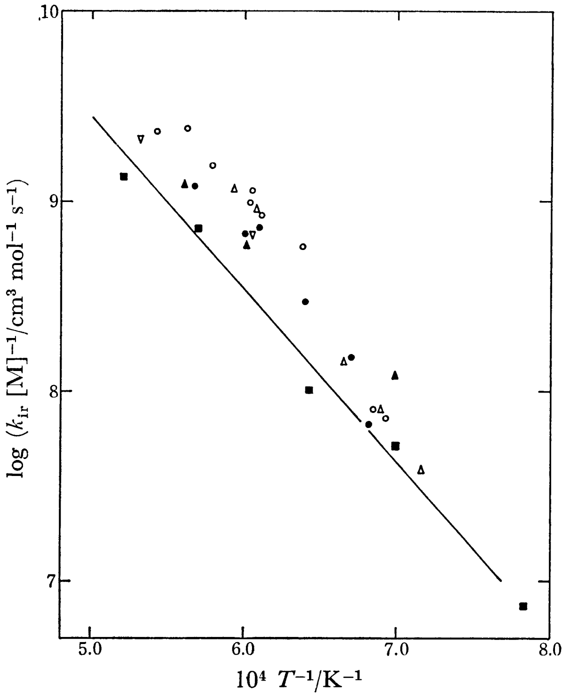

Fig. 5. Arrhenius plot of the second order rate constant k_{ir}/[M] obtained from IR profiles. ▽=3.0%, ▲=1.5%, ○=0.5%, △=0.25%, ●=0.1%, ■=0.03%. Straight line denotes the least square evaluation of k_{2nd} shown in Fig. 4.

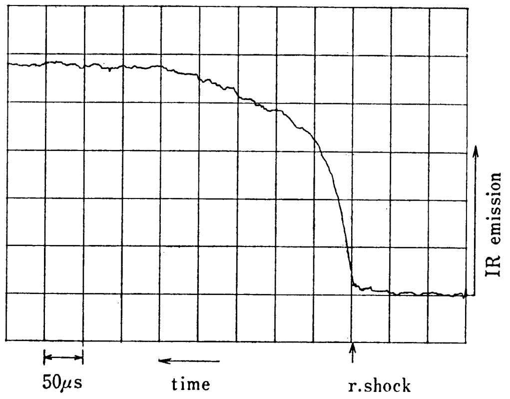

Fig. 6. Typical IR emission profile for the mixture of 0.03% C_2H_3Br in Ar. Temperature=1760 K, total density=1.99×10^{-5} mol cm^{-3}, $k_{ir}/[M]=7.2\times10^8$ cm^3 mol^{-1} s^{-1}.

The IR emission intensity at 3.9 μm is assumed to be proportional to the HBr concentration, since, at this wavelength, there exists no emission by possible products other than HBr. If HBr is produced only by Reaction 1 and does not react subsequently, the time history of the intensity may be expressed as: $I=I_{t=\infty}\{1-\exp(-k_{ir}t)\}$. At first sight, the emission profile seems to follow the above relation. Figure 5 shows the values of k_{ir}/[M] obtained for the various mixtures studied. It may be seen from Fig. 4 that the values of k_{ir}/[M] for mixtures of 0.1—3.0 mol % C_2H_3Br are somewhat larger than those of k_{2nd} (straight line), especially at high temperatures. This implies that, at the later part of the reaction, the dissociation of HBr by secondary reactions cannot be neglected in these relatively high concentration mixtures. That is, the concentration of HBr, $[HBr]_t$, cannot be described by the simple relation: $[HBr]_t=[C_2H_3Br]_0-[C_2H_3Br]_t$ when there is much decomposition. Thus, in order to control the secondary reactions, further experiments were performed for a highly diluted mixture (0.03 mol % C_2H_3Br in Ar). In these additional experiments, the apparatus for the IR observation was modified so as to detect a weak emission. That is, the emission intensity was increased by setting a concave mirror on the opposite side of the tube so as to focus the light on the slit at the detecting side. The emission profile for this mixture is shown in Fig. 6, which is essentially the same as those for the high C_2H_3Br mixtures (Fig. 2(b)). The values of k_{ir}/[M] were obtained again for this series, as plotted in Fig. 5, they show a good agreement with the absorption data (straight line). This suggests that, in highly diluted mixtures such as $[C_2H_3Br]/[Ar]\simeq3\times10^{-4}$, the consumption of HBr by the secondary reactions is negligibly small, even after long reaction times.

Discussion

The initial decomposition rate of vinyl bromide was expressed as first-order in $[C_2H_3Br]$ and first-order in the total density. From the absorption profile, it seems that the decomposition of C_2H_3Br is not so complicated as the chain process, even for mixtures involving a relatively high C_2H_3Br concentration. Also, the fact that the initial rate of the C_2H_3Br consumption is just equal to the HBr production rate for the highly diluted mixture means that the decomposition at the early stage of the reaction occurs *via* a simple reaction. Thus, the following discussion will be made on the basis of the assumption that the decomposition rate constant, $k_{2\mathrm{nd}}$, corresponds to the unimolecular low-pressure-limit rate constant of the primary reaction.

According to the Arrhenius parameters of $k_{2\mathrm{nd}}$, the value of the preexponential factor is somewhat low if the initial process is a single-bond fission, in this respect, the activation energy is much lower than the bond dissociation energy of C–Br, which is the weakest bond in this molecule. This discrepancy (about 35 kcal mol^{-1}) between the activation energy and the bond dissociation energy is too large to be explained by the lower-limit unimolecular process of Reaction 2. If Reaction 2 is the main initiation step, a sequence of rapid consecutive reactions may be expected to occur:

$$C_2H_3(+M) \longrightarrow C_2H_2 + H(+M) \quad (3)$$

$$C_2H_3Br + H \longrightarrow C_2H_3 + HBr \quad (4)$$

$$C_2H_3Br + Br \longrightarrow C_2H_2Br + HBr \quad (5)$$

$$C_2H_2Br(+M) \longrightarrow C_2H_2 + Br(+M). \quad (6)$$

These consecutive reactions would compose a chain cycle and would give rise to an acceleration of the vinyl bromide consumption as the reaction proceeded. In some experiments, such an acceleration was observed in the absorption and emission records at long reaction times and at low temperatures. However, in such cases no unique correlation of the acceleration with the C_2H_3Br concentration could be detected. Therefore, although the possibility of the above reaction scheme (Reactions 2—6) cannot be rejected completely, from the fact that the decomposition rate constant, $k_{2\mathrm{nd}}$, is not changed by the variation in the mixture composition the contribution of the above reactions to the initial decomposition rate may be considered to be negligible under the present conditions. Thus, Reaction 2 is not important as the initiation step.

For Reaction 1 an activation energy much higher than ΔH_r may be expected, as is the case for other well-known four-center reactions. In this case, possible subsequent reactions are the decompositions of acetylene and hydrogen bromide. The unimolecular dissociation of HBr below 2000 K is negligibly small,[6] though, and thus it is not important as the secondary reaction. The decomposition of acetylene has a very high activation energy (124 kcal mol^{-1}),[7] therefore, the effect of the C_2H_2 decomposition is also negligible.

A theoretical calculation of the low-pressure-limit rate constant was performed by using a refinement of the equation of the RRKM theory presented by Troe[8] (Eq. 2.11 in Ref. 8). The molecular constants of C_2H_3Br were taken from Ref. 9, while the parameters appearing in the equation were calculated as in Ref. 10. To obtain the threshold energy, E_0, of the initiation reaction, we first assumed that the collision efficiency, β_c, was constant regardless of the temperature. Thus, we obtained $E_0=55.5$ kcal mol^{-1} when $\beta_c=1.6\times10^{-4}$. This value is the lower limit of E_0, because β_c has a slightly negative temperature dependence.[11] An estimate for the reverse reaction of Reaction 1 according to the semiempirical method by Benson and Haugen[3] leads to 59.5 kcal mol^{-1} for the high-pressure activation energy, $E_{a\infty}$, of Reaction 1 at 1600 K, the middle temperature of the present experiment. Thus, the value of E_0 (55.5 kcal mol^{-1}) obtained as the lower limit seems to be reasonable compared with the value of $E_{a\infty}$. By using this relation: $E_{a0}=E_{a\infty}-(S_{\mathrm{eff}}+0.5)RT$, E_{a0} is calculated to be 41.0 kcal mol^{-1} at 1600 K, where S_{eff}, the number of the effective vibration, is 6.31 at 1600 K. This value of E_{a0} is very close to the experimentally obtained activation energy (41.5 kcal mol^{-1}).

The value of β_c (1.6×10^{-4}) is unexpectedly low compared with that of vinyl chloride ($\beta_c=0.04$).[2] It is recongnized that the unimolecular process of vinyl halides tends toward the low-pressure region as the halogen changes from F to Br under similar conditions, as has been shown by previous experiments[1,2] and also in this work. The fact that the decomposition process of C_2H_3Br is in the low-pressure region is probably the result of the low efficiency of the energy transfer per collision. Nevertheless, at the present time, we cannot explain why, for the C_2H_3Br decomposition, the collision efficiency is extremely small compared with similar reactions.

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10) In the calculation of the strong collision low-pressure rate constant, the following equation was used:

$$k_0^{sc}/[\mathrm{Ar}] = Z_{LJ}\rho_{vib}(E_0)kTQ_{vib}^{-1}\exp(-E_0/RT)F_{rot}F_{anh}F_E.$$

Examples of the data at 2000 K: threshold energy, $E_0=55.5$ kcal mol^{-1}; Lennard-Jones collision frequency, $Z_{LJ}=3.655\times10^{14}$ cm^3 mol^{-1} s^{-1}; vibrational partition function, $Q_{vib}=7.28\times10^1$; harmonic density states at $E_0=7.627\times10^3$; Whitten-Rabinovitch correction factor=0.922; energy dependence of the density of states, $F_E=2.03$; rotational factor, $F_{rot}=1.30$; anharmonicity factor, $F_{anh}=1.20$;

$$k_0^{sc}/[\mathrm{Ar}] = 1.653\times10^{11}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}};$$

$$k_{2nd} = 2.645\times10^7\ \mathrm{cm^3\ mol^{-1}\ s^{-1}};$$

collision efficiency, $\beta_C=1.6\times10^{-4}$.

11) J. Troe, "Proc. 10th Int. Shock Tube Symp.," ed by G. Kamimoto, Kyoto, Japan (1975), p. 29.