Kinetic Study of the Mechanism of the Low-Temperature Pyrolysis of Vinyl Bromide

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The pyrolysis of vinyl bromide has been examined in the temperature range 637−733 K and at pressures from 6 to 86 kPa. The yields of the major hydrocarbon products, C_2H_2, C_2H_4, and 1,3-C_4H_6, are second order in vinyl bromide over the entire range of temperatures investigated. At the higher temperatures, initiation by molecular elimination of HBr dominates, while at lower temperatures a free radical initiation channel becomes increasingly important. Our data for the overall process leading to HBr fit the relation $\ln(k) = (30.7 \pm 4.8) - ((26.6 \pm 3.3) \times 10^3)/T$, with the rate constant in the units L mol^{-1} s^{-1}, indicating an activation energy of 220 kJ mol^{-1} ± 12% for the HBr elimination. A simple Arrhenius extrapolation is close to previous results at temperatures from 800 to over 2000 K. The combination of our data and the earlier measurements of the HBr elimination is reasonably represented by $\ln(k) = 37 - (3 \times 10^4)/T$. Our data suggest that the free radical pathway is disproportionation rather than unimolecular cleavage of the C−Br bond, a situation analogous to that in the low-temperature thermal decomposition of ethylene. Kinetic analysis indicates that the activation energy of this new free radical initiation channel is approximately 150 kJ mol^{-1}, much less than the C−Br bond energy.

Introduction

The vinyl radical figures prominently as a reactive intermediate in a wide range of chemical processes, including combustion and petroleum refining operations such as cracking. It has also been implicated in the formation of soot in flames and in the deposition of carbon in industrial pyrolysis systems. Its chemistry is of fundamental importance too since it is the simplest unsaturated free radical. Despite its importance, very few good sources of the vinyl radical are available for kinetic or mechanistic work. Those sources that have been examined frequently are accompanied by parallel complicating reactions that reduce the yield of vinyl radicals and introduce species that interfere with the vinyl radical chemistry one would like to study. Direct measurement of this radical by nondestructive methods such as optical spectroscopy remains difficult due to relatively low detection sensitivity and interference due to absorption of light by the precursor or by other species that are formed at the same time. The high chemical reactivity of the vinyl radical also imposes a limit on the concentrations that can be obtained from many sources.

In view of their importance in combustion and industrial pyrolysis, it is desirable to identify a source of vinyl radicals that could be used for kinetic and mechanistic experiments at temperatures of a few hundred degrees Celsius. Preliminary experiments in our laboratory to evaluate the range of temperatures over which vinyl bromide could be used as a photochemical source of vinyl radicals indicated that a free radical thermal decomposition process became important at temperatures above approximately 350 °C. A survey of the literature indicated that the only thermal decomposition process that has been identified experimentally is the molecular elimination of HBr.[1−4] The experiments that have been reported were all done at comparatively high temperatures.

Shilov and Sabirova[1] studied the decomposition of C_2H_3Br from approximately 900 to 1100 K at pressures of 1−7 kPa, using the toluene jet technique. They found that the reaction was kinetically second order and did not depend on the surface/volume ratio. Their results were independent of whether toluene or benzene was used in the jet. They observed ethylene as well as acetylene in the decomposition of C_2H_3I but only acetylene in the decomposition of C_2H_3Br and took this to indicate that only the molecular decomposition of C_2H_3Br to C_2H_2 and HBr was significant. They reported an activation energy of 274 kJ mol^{-1} and a preexponential factor of 1.0×10^{17} L mol^{-1} s^{-1} for the molecular decomposition.

Cadman and Engelbrecht[2] studied the decomposition of C_2H_3Br in a reflected shock wave at temperatures from 1630 to 2100 K. They assumed that the decomposition was unimolecular and found no evidence for any channel other than the one giving acetylene and HBr. They reported an activation energy of 262 kJ mol^{-1} but, since this was a brief note, they did not provide enough experimental information to permit calculation of a bimolecular preexponential factor from their reported unimolecular value of 9.5×10^{12} s^{-1}.

Lippiatt and Wells[3] studied the reaction in a shock tube coupled to a time-of-flight mass spectrometer at temperatures from 1329 to 2128 K at pressures close to 20 kPa. They found only C_2H_2 and HBr as products of the reaction and reported that the rates of formation of these products mirrored the rate of disappearance of C_2H_3Br. The activation energy was reported to be 160 kJ mol^{-1} with a bimolecular preexponential factor of 1.0×10^{12} L mol^{-1} s^{-1}.

The most recent investigation of the decomposition of C_2H_3Br also used a reflected shock wave.[4] The reaction was studied from 1300 to 2000 K at pressures of a few hundred kilopascals. They considered the possibility of a channel giving C_2H_3 + Br but found no evidence for it. They concluded that the decomposition of C_2H_3Br occurred entirely by the molecular channel giving C_2H_2 and HBr and reported an activation energy of 174

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kJ mol^{-1} with a preexponential factor of 9.5 × 10^{10} L mol^{-1} s^{-1} for this reaction.

While the thermal decomposition of C_2H_3Br has been studied from approximately 900 to over 2000 K, no evidence has been reported for a decomposition channel other than the molecular one leading to C_2H_2 and HBr. This contrasts with our observation of substantial yields of C_2H_4 and 1,3-C_4H_6 in the decomposition at temperatures as low as 630 K, suggesting the occurrence of a free radical decomposition channel that produces C_2H_3 radicals. There is also some disagreement concerning the activation energy for the molecular process. We have therefore undertaken an experimental study of the lower temperature decomposition of vinyl bromide below 800 K to measure the relative importance of the molecular and free radical channels and to clarify the kinetics and mechanism of the free radical process. We report here a kinetic analysis of our data which separates the molecular and free radical channels and provides an empirical kinetic characterization of each.

Experimental Section

The pyrolysis experiments were made in Pyrex reaction vessels that were heated electrically and were well-insulated. The surface/volume ratios of these reactors ranged from 1.0 to 11 cm^{-1}. The temperature was monitored continuously with calibrated iron–constantan thermocouples that were inserted into thermocouple wells extending into the center of the pyrolysis vessel. The temperature remained constant during an experiment to within the measurement precision which was better than ±0.5%. Pressures were measured with piezoelectric pressure transducers whose calibration was checked daily. Kinetic measurements made under identical conditions in different reaction vessels were indistinguishable.

Experiments were all made in batch mode. A reaction mixture of known composition was introduced to the reaction vessel at a measured pressure. It was then allowed to react for a measured length of time that was at least 10 times the settling time for the pressure. At the end of the desired reaction time, a measured pressure of the reaction mixture was transferred to a gas sample loop and injected onto the chromatographic column. This procedure prevented loss of products such as ethylene that do not trap quantitatively with liquid nitrogen. When reactions required the use of mixtures of vinyl bromide with other gases such as argon, the gases were added to a reservoir at known pressures and were allowed to mix for a sufficiently long time that experiments using both longer and shorter mixing times gave identical results.

The reaction mixtures were analyzed by gas chromatography using either a Perkin-Elmer Sigma 3 or a Hewlett-Packard HP5880 gas chromatograph. Both instruments used a flame ionization detector, and the HP5880 was also interfaced to a Ametek Dycor MA200M quadrupole mass spectrometer. Most of the analyses used a 30 foot, $^1/_8$ in. diameter column packed with SP1700, but a few analyses used columns packed with Carbosieve G, Porapak Q, or Hayesep T to verify acceptable resolution of the components to be analyzed in the reaction mixtures. The chromatographs were calibrated daily with gas mixtures containing known amounts of the desired analytes diluted in helium. Typical chromatographic conditions with the SP1700 column were 75 psi helium carrier, temperature program 50 °C for 20 min, ramp to 70 °C at 10 °C/min, and hold at 70 °C for 30 min. Typical retention times under these conditions were as follows: ethylene, 6.5 min; acetylene, 8.7 min; 1,3-butadiene, 20.7 min; vinyl bromide, 46 min. The identities of the reaction products were determined initially by comparison of their chromatographic retention times with those of authentic samples, and these identifications were confirmed by obtaining the mass spectra of the individual product peaks as they eluted from the chromatographic column. The resolution of the products was also checked by observing the mass spectra obtained during successive scans of the mass spectrum as a given peak eluted from the column.

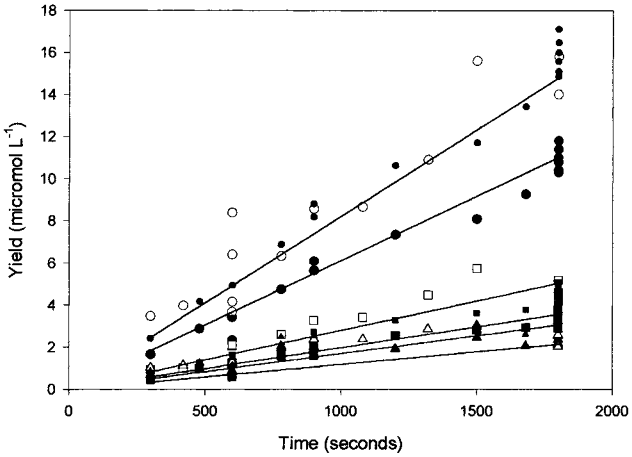

Figure 1. Effect of varying the surface/volume ratio. Open symbols are for the unpacked reaction vessel, S/V = 1.0 cm^{-1}, at a temperature of 711 ± 2 K and a pressure of 16.1 ± 0.4 kPa of C_2H_3Br. The larger closed symbols are for the packed reaction vessel, S/V = 11 cm^{-1}, at a temperature of 704 ± 2 K and a pressure of 16.2 ± 0.6 kPa of C_2H_3-Br. The smaller closed symbols are for the packed reaction vessel, corrected to refer to the temperature of 711 K used in the unpacked reaction vessel, using the experimental activation energies for each of the reaction products. ○, ●, C_2H_2: □, ■, C_2H_4: △, ▲, 1,3-C_4H_6.

Vinyl bromide was obtained from the Aldrich Chemical Co. and had a stated purity of 98%. It contained methyl ethyl hydroquinone as an inhibitor. It was purified before use by freeze–pump–thaw cycles followed by bulb to bulb distillation retaining only the middle part. Gas chromatographic analysis of the purified material on the SP1700 column gave only a single peak, while analysis on the Hayesep T column gave a small additional peak, representing about 0.2% of the C_2H_3Br peak, with a retention time slightly less than that of the C_2H_3Br peak. This additional peak did not interfere with those of the reaction products being measured and its area, relative to that of the C_2H_3Br peak, did not change when the vinyl bromide was pyrolized. It was concluded that the substance responsible for the small additional peak when the Hayesep T column was used for analysis did not affect either the chemical analysis or the chemical behavior of the reaction under study.

Results and Discussion

Ethylene, acetylene, 1,3-butadiene, and vinyl acetylene were the hydrocarbon reaction products obtained in the experiments. Their yields were measured as a function of both the pressure of vinyl bromide and reaction time at each temperature. The extent of decomposition of vinyl bromide was at most 5% and in most cases was much less than this. While HBr is presumably formed in the reaction, we were not able to detect it or measure its concentration with the available instrumentation. Representative plots of product yields as a function of reaction time are shown in Figures 1 and 2. The standard deviations of the points on such plots were typically of the order of 10–25%, depending on the temperature, specific reaction product, and extent of

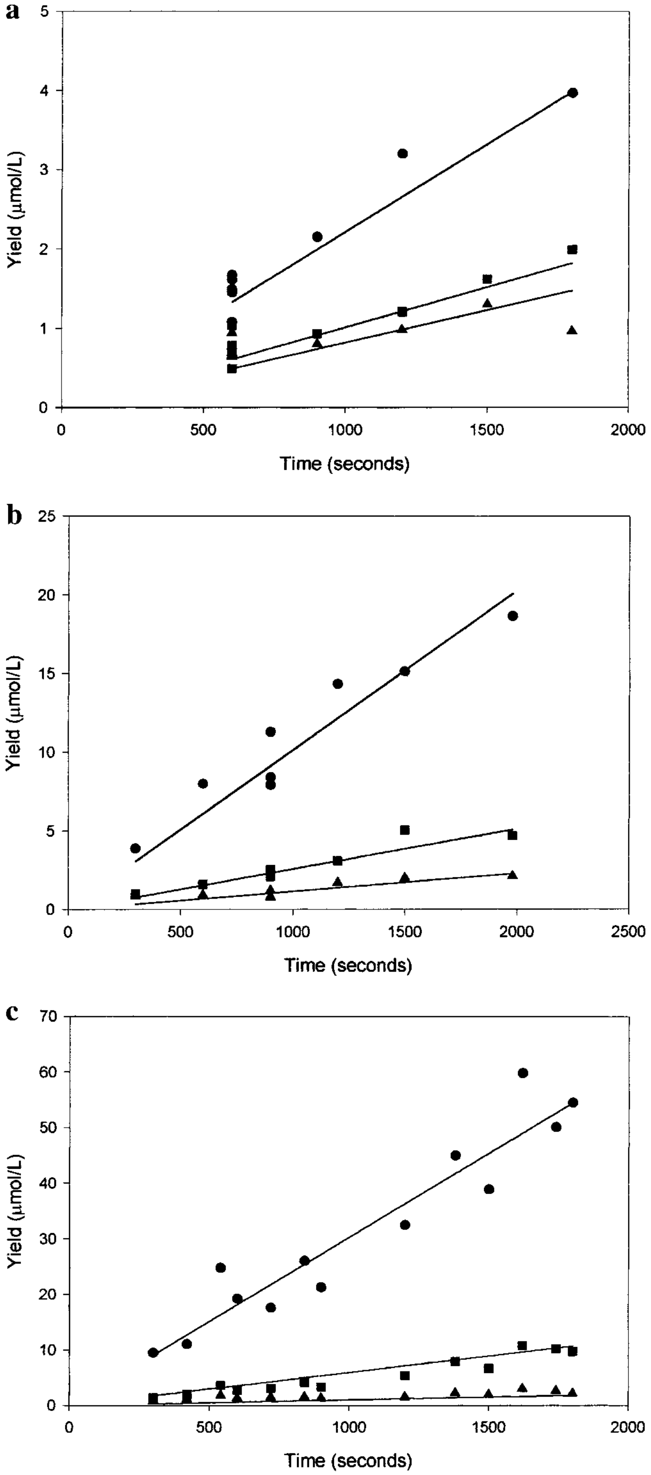

Figure 2. (a) Representative plots of the dependence of product yields on reaction time at a total pressure of 16 kPa and (a, top) 636, (b, middle) 711, and (c, bottom) 734 K: ●, C_2H_2; ■, C_2H_4; ▲, 1,3-C_4H_6.

reaction. When replicate experiments were made, their standard deviations were also of this magnitude.

Chromatograms of the mixture of reaction products usually showed a small, unresolved peak with a retention time approximately 4 min longer than that of vinyl bromide. Sequential scans with the mass spectrometer as this unresolved peak eluted from the SP1700 column gave a series of peaks at masses of 186, 188, and 190 with the intensity ratio to be expected of a dibrominated compound. The masses and intensity distribution of these peaks in the mass spectrum indicated that $C_2H_4Br_2$ was probably present in the reaction products but was not resolved on this chromatographic column from the very much larger peak due to unreacted vinyl bromide at the small conversions of vinyl bromide used in our experiments. Similar GC/MS experiments with purified vinyl bromide gave no indication of the presence of $C_2H_4Br_2$, and the gas chromatogram gave no indication of the unresolved peak in the tail of the vinyl bromide peak.

While the incomplete resolution of the chromatographic peak tentatively assigned to $C_2H_4Br_2$ prevented its quantitation and limited the detail that could be obtained in its mass spectrum, a few analyses were made of mixtures of vinyl bromide with 1,2-dibromoethane to assess the likelihood that these results could reasonably be attributed to an isomer of $C_2H_4Br_2$. Gas chromatograms of mixtures of vinyl bromide and 1,2-dibromoethane also showed an incompletely resolved peak in the tail of the peak due to vinyl bromide. This unresolved peak had the same retention time as the unresolved peak, tentatively attributed to dibromoethane, in the reaction products. Although the poor resolution of this peak from that due to vinyl bromide prevented its use for analytical purposes, the combination of the gas chromatographic and mass spectrometric measurements is consistent with the formation of 1,2-dibromoethane as a product of the thermal decomposition of vinyl bromide under our conditions. These limited experiments do not rule out the possibility that 1,1-dibromoethane is formed as well, but the limited resolution of the peak attributed to $C_2H_4Br_2$ from the tail of the peak for vinyl bromide suggested that a more complete series of experiments was unlikely to provide additional significant information. Vinyl acetylene was a significant reaction product only at the higher temperatures. It was identified by its mass spectrum, but we were unable to obtain a sample of the authentic material to use for calibration of the gas chromatograph.

Figure 1 shows yields of products as a function of reaction time obtained at approximately the same temperature and pressure in reaction vessels of widely different surface/volume ratios. The open plotting symbols, representing the results for the reaction vessel with the small *S*/*V* ratio, lie consistently above the filled plotting symbols, representing the results obtained in the reaction vessel with the larger *S*/*V* ratio. However, the results represented by the open plotting symbols were also obtained at a temperature 7 ± 4 °C higher than that at which the data for the filled plotting symbols were obtained. When the measured variation of yields with temperature is considered, the small increase in yield in the reaction vessel having the small *S*/*V* ratio is entirely accounted for by the slightly higher reaction temperature used with that reaction vessel. This is indicated by the smaller filled plotting symbols in Figure 1. These represent product yields that were corrected for the small variation in temperature using the activation energy for each product obtained from the data presented in Figures 6−8. The results obtained with reaction vessels of different *S*/*V* ratios suggest that surface effects are negligible in our experiments.

Figure 2 shows representative plots of the variation of product yields with time in the upper, lower, and middle parts of the temperature range examined. The yield of acetylene is clearly the largest over the entire temperature range. However, its yield becomes proportionately smaller as the temperature decreases. In contrast, the ratio of yields of the more minor products, ethylene and 1,3-butadiene, shows much less variation with temperature. This suggests that the kinetically limiting processes leading to acetylene are different from those leading to ethylene and butadiene and that the kinetically limiting processes leading to the latter two products are similar. The plots of which those in Figure 2 are representative were all linear over the range of

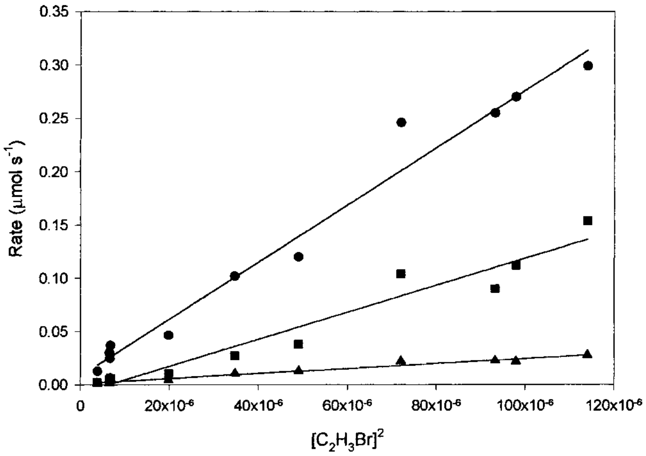

Figure 3. Representative plots to verify second-order dependence on [C_2H_3Br]. The temperature for these experiments was 732 K: ●, C_2H_2: ■, C_2H_4: ▲, 1,3-C_4H_6.

temperatures, pressures, and reaction times investigated, indicating that secondary reactions involving the measured reaction products were either negligible or had a constant stoichiometric effect on the measured yields. We conclude from this behavior that, at the small conversions of C_2H_3Br in our experiments, the slopes of such plots give reasonable estimates of the initial rates of formation of the reaction products.

Reaction rates were measured as a function of initial concentration of vinyl bromide over the full range of temperatures studied. The concentration of vinyl bromide was varied by roughly an order of magnitude in these experiments. Plots of reaction rate against the square of the vinyl bromide concentration were accurately linear for each of the measured reaction products. The formation of each of these products is therefore second order in vinyl bromide, and empirical second-order rate constants can be calculated by dividing the initial rate by the square of the vinyl bromide concentration. A representative set of such plots is shown in Figure 3. The precision of the individual data points in such plots was of the order of 10−25%, depending on reaction conditions. The precision of the slopes of plots such as those in Figure 3 was also of this magnitude. Experiments were also made in which the pressure of vinyl bromide was kept constant while the total pressure was increased by adding argon. If the second-order behavior is due to reactions requiring energy transfer from the bath gas, the empirical second-order rate constants will increase as the argon pressure is increased. However, if the second-order kinetic behavior is due to a chemical interaction between two vinyl bromide molecules rather than energy transfer, the second-order rate constants should be independent of the pressure of added argon. The data in Figure 4 indicate that the rate constants based on the yields of C_2H_4 and 1,3-C_4H_6 are independent of the pressure of added argon while the rate constants based on the yield of C_2H_2 depend strongly on the pressure of added argon. These results indicate that some reactions that have kinetic control over the yield of C_2H_2 depend on energy transfer while the reactions leading to C_2H_4 and 1,3-C_4H_6 result from a chemical interaction between two molecules of C_2H_3Br. The second-order behavior of the rate of production of C_2H_2 is consistent with the results of three of the literature reports[1,3,4] in which the effect of pressure on the measured rate constant for formation of C_2H_2 was examined, and the reaction was found to be second order under their conditions.

We must first evaluate the possible initiation steps in the decomposition of vinyl bromide. It was noted earlier that the only thermal decomposition channel that has been reported experimentally is

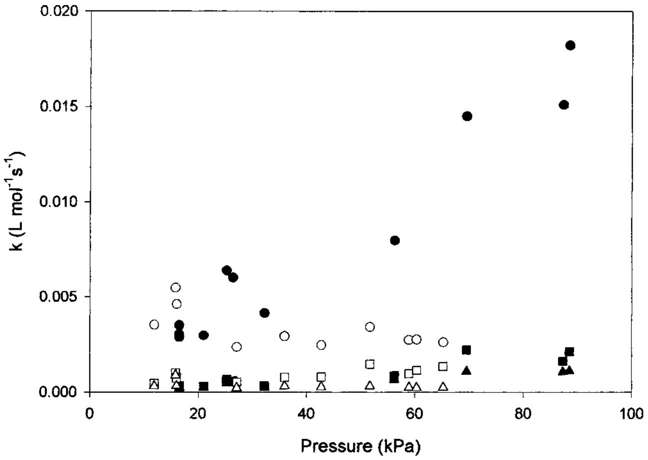

Figure 4. Effect of replacing C_2H_3Br with Ar as a bath gas. The filled symbols are for experiments with 16 kPa of C_2H_3Br and varying pressures of added Ar. The open symbols are for experiments with pure C_2H_3Br. The temperature for these experiments was 732 K. ○, ●, C_2H_2; □, ■, C_2H_4; △, ▲, 1,3-C_4H_6.

$$C_2H_3Br \rightarrow C_2H_2 + HBr \tag{1}$$

The observation of large yields of C_2H_2 in our work is consistent with this being an important decomposition process.

The reaction

$$C_2H_3Br \rightarrow C_2HBr + H_2 \tag{2}$$

has been reported in matrix isolation work.[5,6] A careful search for H_2 as a product in our experiments, using a gas chromatograph equipped with a 5A molecular sieve column and a thermal conductivity detector, was negative. Our detection limits indicated that we should have been able to detect H_2 at a concentration of at least 0.8 μmol/L. We conclude on this basis that channel 2 does not occur significantly under our conditions. This also indicates that the channel

$$C_2H_3Br \rightarrow C_2H_2 + H + Br \tag{3}$$

does not take place appreciably since the hydrogen atom produced in this reaction would almost certainly lead to formation of H_2, either as a result of hydrogen abstraction from vinyl bromide or by recombination. These results are consistent with the conclusion of a theoretical analysis of decomposition of vinyl bromide on the ground-state potential energy surface[7] in which HBr elimination was found to have a potential barrier approximately 100 kJ mol^{-1} lower than H_2 elimination and even farther below reaction 3.

The observation of significant quantities of ethylene, 1,3-butadiene, and vinyl acetylene as reaction products leads to the conclusion that a free radical initiation process that forms vinyl radicals must be occurring. The initiation reaction

$$C_2H_3Br \rightarrow C_2H_3 + Br \tag{4}$$

would provide the necessary free radicals for a chain process leading to the observed products. This would then be followed

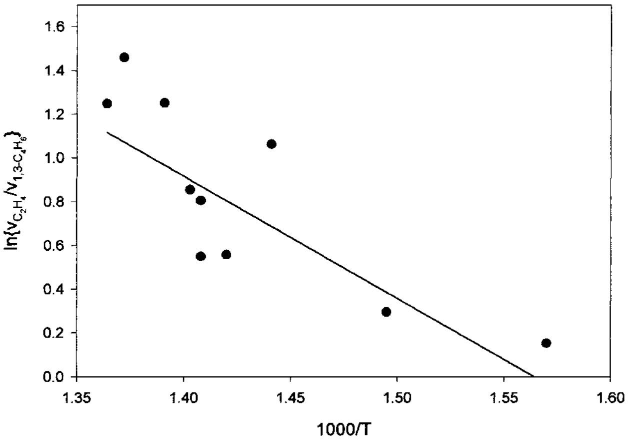

Figure 5. Temperature dependence of the ratio of the rate of formation of C_2H_4 to that of 1,3-C_4H_6.

by the reactions below, leading to C_2H_4 and additional C_2H_2

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br \quad (5)$$

$$Br + C_2H_3Br \rightarrow HBr + C_2H_2Br \quad (6)$$

$$C_2H_2Br \rightarrow C_2H_2 + Br \quad (7)$$

as well as the following reactions giving 1,3-C_4H_6

$$Br + C_2H_3Br \rightarrow C_2H_3Br_2 \quad (8)$$

$$C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br \quad (9)$$

$$C_4H_6Br \rightarrow 1,3\text{-}C_4H_6 + Br \quad (10)$$

$$2\ C_2H_3 \rightarrow 1,3\text{-}C_4H_6 \quad (11)$$

The relative importance of reactions 10 and 11 can be inferred from the temperature dependence of the ratio of rates of formation of C_2H_4 and 1,3-C_4H_6. The relevant data are shown in Figure 5. The data are more scattered than those for the Arrhenius plots of Figures 6−8 because the latter depend on the measurement of the yield of only one reaction product while the data of Figure 5 require the yields of two reaction products of comparable magnitude. However, it is clear that the ratio of rates, $\nu_{C2H4}/\nu_{1,3-C4H6}$, increases with increasing temperature. The slope of the line in Figure 5 leads to an energy of 46 kJ mol^{-1} ± 31%, which represents the difference in activation energy of the reaction paths leading to C_2H_4 and 1,3-C_4H_6.

We first examine the formation of 1,3-C_4H_6 via reactions 9 and 10. If it is assumed that reaction 5 determines the proportion of C_2H_3 that produces C_2H_4 while reaction 9 determines the proportion of the channel leading to 1,3-C_4H_6, the ratio of rates $\nu_{C2H4}/\nu_{1,3-C4H6}$ should be approximately equal to the ratio k_5/k_9. Since reaction 5 is a hydrogen abstraction while reaction 9 is a free radical addition, reaction 5 should have the larger activation energy and the ratio of rates should increase with increasing temperature as observed. The slope of the plot in Figure 5 would then represent the difference in activation energy of reactions 5 and 9. While kinetic data for reactions of C_2H_3 are scarce, the difference in activation energy for the comparable abstraction and addition reactions of C_2H_3 with C_3H_6 has been estimated[8] to be approximately 26 kJ mol^{-1}, which is similar to the value estimated from the slope of Figure 5. As an alternative comparison, the difference in activation energies for the addition and abstraction reactions of C_2H_5 with C_2H_4 is[9] 40 kJ mol^{-1}, which is also similar to the value derived from Figure 5. The temperature dependence of the relative rates of formation of C_2H_4 and 1,3-C_4H_6 seems to be qualitatively consistent with reactions 9 and 10 as the main source of 1,3-C_4H_6.

We next consider the alternative of reaction 11 as the dominant source of 1,3-C_4H_6. In that case, the ratio of rates of formation of C_2H_4 and 1,3-C_4H_6 would be given by

$$\frac{\nu_{C_2H_4}}{\nu_{1,3-C_4H_6}} = \frac{k_5[C_2H_3Br]}{k_{11}[C_2H_3]}$$

In this case, the activation energy obtained from the relative rate measurements would reflect the difference $E_a(5) - E_a(11) - E_a(C_2H_3)$. Reaction 11 is a simple recombination reaction and is expected to have no activation energy. The activation energy for production of C_2H_3, $E_a(C_2H_3)$, is expected to be comparable to that for the initiation reaction producing C_2H_3 and should be substantially larger than that for reaction 5. If reaction 11 were the main source of 1,3-C_4H_6, the ratio of rates for C_2H_4 and 1,3-C_4H_6 should either be nearly independent of temperature or should decrease with increasing temperature. We conclude that the temperature dependence of the relative rates of formation of C_2H_4 and 1,3-C_4H_6 is more consistent with the principal formation of 1,3-C_4H_6 through reactions 9 and 10 than with its formation in reaction 11.

The basic reaction scheme above suggests that decomposition of the C_2H_2Br radical provides a source of C_2H_2 in addition to that arising from reaction 1. There are two sources of this radical, reactions 5 and 6. Assuming that decomposition of C_2H_2Br in reaction 7 is rapid and that reaction 5 is the only significant source of C_2H_4, the yield of C_2H_4 provides an estimate of the additional C_2H_2 produced via (5) and (7). There is no comparable way of estimating the extra C_2H_2 produced via (6) and (7) since no unique products result. However, examination of the literature on reactions of olefins with halogen atoms leads one to the conclusion that the addition process, reaction 8, is likely to dominate the abstraction process, reaction 6, by at least an order of magnitude (see, for example, refs 9−11). With this assumption, one may estimate the yield of C_2H_2 from reaction 1 by subtracting the yield of C_2H_4 from the measured total yield of C_2H_2. The plots of net C_2H_2, calculated in this way, against reaction time were linear, and their slopes were divided by the square of the C_2H_3Br concentration to obtain estimates of the second-order rate constant for reaction 1.

Figure 6 presents our kinetic data for reaction 1 in Arrhenius format and provides an inset for comparison with the earlier studies in which second-order rate constants were reported. Our results yield a preexponential factor of 2.5 × 10^{13} L mol^{-1} s^{-1} and an activation energy of 220 kJ mol^{-1} ±13%. This degree of uncertainty in the slope of Figure 6 gives a large extrapolation uncertainty in determining the preexponential factor and is a result of the limited temperature range accessible in our experiments. This makes our estimate above of the preexponential factor quite approximate. Our experimental values may be compared with those of Shilov and Sabirova[1] (1.0 × 10^{17} L mol^{-1} s^{-1} and 274 kJ mol^{-1}), Lippiatt and Wells[3] (1.0 × 10^{12} L mol^{-1} s^{-1} and 163 kJ mol^{-1}), and of Saito et al.[4] (9.5 × 10^{13} L mol^{-1} s^{-1} and 170 kJ mol^{-1}) obtained at much higher temperatures. As shown in the inset of Figure 6, our data and those of the three earlier studies cluster about a straight line which gives a preexponential factor of 8.2 × 10^{15} L mol^{-1} s^{-1} and an activation energy of 250 kJ mol^{-1}. While it is clear that these data could also be accommodated by a line with gentle upward curvature, the quality of the data does not justify more than a linear representation. The agreement between our results

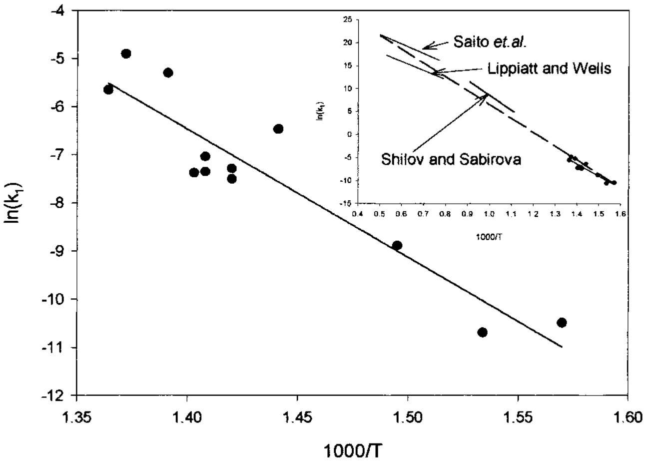

Figure 6. Temperature dependence of the rate constants estimated for reaction 1. The inset compares our results with the kinetic data reported from earlier work done at much higher temperatures. The dashed line provides a composite representation of our work and that of the three earlier studies.

and the earlier work is good, particularly considering the lengthy extrapolation involved, the limited temperature range accessed by our experiments, the extent of disagreement between the two shock tube studies, the variety of experimental methods used, and our indirect method of estimating the rate constant for reaction 1.

While the principal objective of this work is the separation and experimental characterization of the free radical component of the thermal decomposition of vinyl bromide at comparatively low temperatures, the nature of the HBr elimination path requires some comment. Although this has traditionally been regarded as a four-center elimination, there is now a significant body of work indicating that the three-center elimination of HBr is a lower energy reaction path. This includes both experimental work[12−14] using infrared multiphoton dissociation (IRMPD) of vinyl halides and theoretical calculations on an analytic potential energy surface for vinyl bromide.[7,15] While IRMPD accesses higher energies than conventional pyrolysis experiments such as ours, it presumably still occurs on the ground-state potential surface, and many of the conclusions reached from these studies should still be relevant to thermal activation experiments.

While a four-center decomposition process would be completely molecular, producing HBr and acetylene, a three-center decomposition would yield HBr and vinylidene. The isomerization of vinylidene to acetylene has a low energy barrier estimated to be in the range[7] of 19.7−2.3 kJ mol^{-1}, indicating that it is likely to be rapid relative to the three-center process. The overall decomposition process leading to HBr and acetylene would then comprise the reactions

$$C_2H_3Br \rightarrow CH_2C\!: + HBr \tag{12}$$

$$CH_2C\!: \rightarrow CHCH \tag{13}$$

in which our experiments indicate that reaction 12 would be in its second-order regime. The possible intervention in our experiments of reactions initiated by vinylidene needs to be examined. The key question is whether the isomerization reaction is sufficiently rapid that reaction 13 dominates over alternative loss routes for vinylidene.

The shock tube[2−4] and toluene jet[1] experiments did not report any products other than HBr and acetylene. The IRMPD experiments on vinyl halides also were unable to detect products other than acetylene that could have resulted from vinylidene, although experiments with vinyl fluoride[13] observed infrared emission from vibrationally excited acetylene. They found that this emission was consistent with the approximately 170 kJ mol^{-1} of the exothermicity of reaction 13, which they took as evidence that the initial decomposition gave vinylidene that rapidly isomerized to acetylene. Recent IRMPD experiments on vinyl bromide[14] found only acetylene, HBr, and a noncondensable gas, which was assumed to be hydrogen, under their normal irradiation conditions. When the laser was tightly focused, diacetylene and a black soot deposit were found but these products were absent in experiments with a long focal length lens. Both the thermal activation experiments[1−4] and the IRMPD work[12−14] access higher energies than our experiments, and one might expect them to produce larger yields of vinylidene than would be obtained in our work. The absence of stable reaction products that could be attributed to vinylidene in the higher energy experiments suggest that vinylidene isomerizes so rapidly that there was insufficient time to produce stable products in bimolecular reactions.

Vinylidene is thought to be formed in its singlet state and would be expected to undergo rapid addition to compounds such as vinyl bromide. The adduct might then decompose giving HBr and C_4H_4, vinyl acetylene, which was observed in our experiments but for which quantitative measurement was not possible. It would not, however, be expected that vinylidene would produce either ethylene or 1,3-butadiene in the quantities that were measured. It should be noted that the chromatographic peaks for vinyl acetylene were no larger than those for 1,3-butadiene, the product formed in the smallest amount, and were usually much smaller. The main effect of such reactions would be to make the extent of the HBr elimination reaction estimated from the acetylene yield too small. This, in turn, would make our estimates of the rate constants for that reaction too small. The observation that our kinetic data for the HBr elimination extrapolate well to those obtained at the much higher temperatures of the shock tube and toluene jet experiments, as indicated in Figure 6, suggests that our assumption that vinylidene isomerizes to acetylene so rapidly that it does not participate appreciably in other reactions in the system is not seriously in error. The formation of vinyl acetylene in our system can equally well be accounted for by the reaction of C_2H_3 with acetylene, as discussed later.

We now turn our attention to the free radical component of the reaction. If reaction 4 is kinetically limiting for production of C_2H_3, the subsequent reactions consuming C_2H_3 should yield products whose kinetic behavior contains information about reaction 4. We first consider C_2H_4. This is produced in the reaction sequence

$$C_2H_3Br \rightarrow C_2H_3 + Br \tag{4}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br \tag{5}$$

The formation of C_2H_4 was found to be second order in C_2H_3Br, so the initial rate of formation of C_2H_4 divided by the square of the concentration of C_2H_3Br will give an effective rate constant which, when plotted in Arrhenius form, will yield information about the kinetically limiting step. Such a plot is found in Figure 7. While the intercept of such a plot has no simple interpretation since it does not necessarily describe a single elementary reaction, the activation energy should reflect that of the kinetically limiting step. The activation energy of reaction 4, as written, should be comparable to the C−Br bond energy, which has been estimated[16] to be about 320 kJ mol^{-1}, while that of reaction 5 should be roughly[9] 20−30 kJ mol^{-1}.

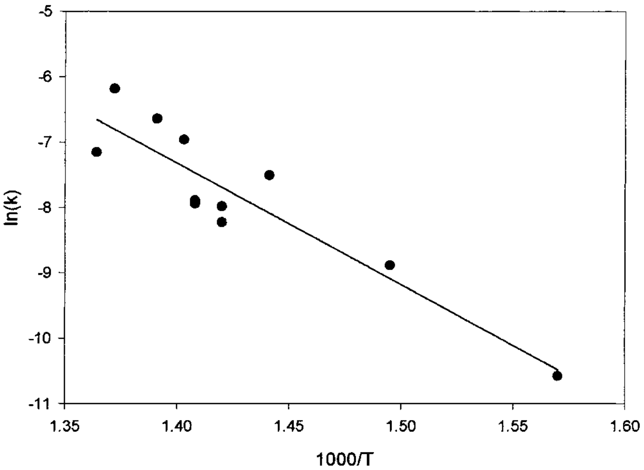

Figure 7. Temperature dependence of the empirical second order rate constants based on the rate of formation of C_2H_4.

Reaction 4 would therefore be kinetically limiting for C_2H_4, and the activation energy for production of C_2H_4 would be roughly 300 kJ mol^{-1} if reaction 4 were a unimolecular C−Br bond scission. The slope of the plot in Figure 7 gives an activation energy of 150 kJ mol^{-1} ± 14%. This, together with the measured reaction order of 2, suggests that the source of C_2H_3 is not the unimolecular dissociation of C_2H_3Br as presented in reaction 4.

A similar conclusion can be reached by examining the yields of 1,3-C_4H_6. The production of 1,3-C_4H_6 was found to be second order in C_2H_3Br, so an empirical second-order rate constant can be calculated by dividing the measured initial rate of formation of 1,3-C_4H_6 by the square of the concentration of C_2H_3Br. Figure 8 shows the temperature dependence, in Arrhenius format, of these empirical rate constants based on the formation of 1,3-C_4H_6. The slope of the line in this plot gives an activation energy of 136 kJ mol^{-1} ± 15%, a value that is comparable with that obtained from the rates of formation of C_2H_4 and again much smaller than the C−Br bond energy in C_2H_3Br. The minimum set of chemical reactions required to produce 1,3-C_4H_6 in this system is similar to that for production of C_2H_4, namely,

$$C_2H_3Br \rightarrow C_2H_3 + Br \quad (4)$$

$$C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br \quad (9)$$

$$C_4H_6Br \rightarrow 1,3\text{-}C_4H_6 + Br \quad (10)$$

The activation energy of reaction 9 is expected[9] to be of the order of 10−20 kJ mol^{-1}, while that for reaction 10 is expected[9] to be of the order of 20−30 kJ mol^{-1}. Again, the activation energy for the production of 1,3-C_4H_6 should be dominated by that of reaction 4 and would be roughly 300 kJ mol^{-1} if C_2H_3 radicals were to result from unimolecular dissociation of C_2H_3Br. Clearly a lower energy pathway must be responsible for production of the vinyl radical in this system.

A similar situation exists in the pyrolysis of ethylene for which the initiation step has been found to be second order with a measured activation energy of approximately 240 kJ mol^{-1},[17,18] much less than the C−H bond energy in C_2H_4. It has been suggested[19,20] that the pyrolysis of ethylene occurs by a different mechanism at the high temperatures of shock tube experiments than at the lower temperatures of conventional pyrolysis experiments and that, below roughly 1000 K, initiation is strongly dominated by disproportionation to ethyl and vinyl radicals. Under shock tube conditions, on the other hand, initiation is dominated by direct C−H bond cleavage with its much larger activation energy and larger preexponential factor. This view is consistent with recent detailed kinetic modeling of ethylene pyrolysis in the lower temperature regime.[21,22]

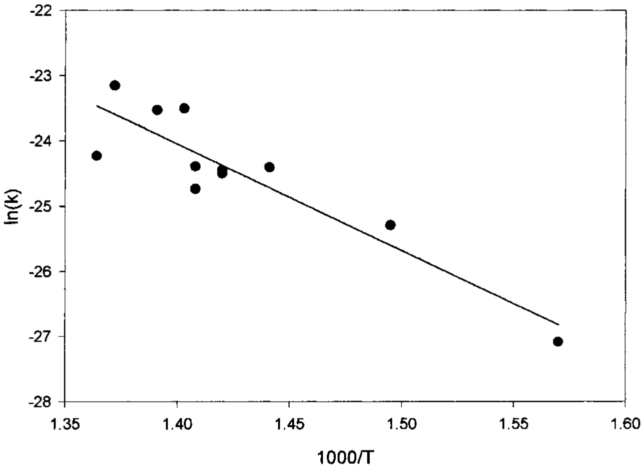

Figure 8. Temperature dependence of the empirical second-order rate constants based on the rate of formation of 1,3-C_4H_6.

The unexpectedly small activation energy for initiation of the free radical component of the pyrolysis of vinyl bromide is consistent with a similar explanation. Reaction 4 is stoichiometrically equivalent to the following sequence of reactions.

$$2C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2 \quad (14)$$

$$C_2H_3Br_2 \rightarrow C_2H_3Br + Br \quad (15)$$

As with reaction 10, the activation energy for reaction 15 is anticipated[9] to be in the range of 20−30 kJ mol^{-1} and reaction 14 would be responsible for the larger value of about 140−150 kJ mol^{-1} which we measure for the production of 1,3-C_4H_6 and C_2H_4. Reaction 14 would then be the rate-limiting step and would result in the second-order kinetics observed for production of C_2H_4 and 1,3-C_4H_6. Since reaction 14 requires a chemical interaction between two C_2H_3Br molecules, its rate constant should not depend appreciably on energy transfer from the bath gas. This is consistent with our observation that the rate constants calculated from the rates of formation of C_2H_4 and 1,3-C_4H_6 do not depend on whether the bath gas is argon or C_2H_3Br. The tentative identification of $C_2H_4Br_2$ by its mass spectrum in the effluent from the gas chromatograph, referred to at the beginning of this section, would also be consistent with the occurrence of reactions 8 and 14.

$$Br + C_2H_3Br \rightarrow C_2H_3Br_2 \quad (8)$$

$$2C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2 \quad (14)$$

The $C_2H_3Br_2$ radical formed in these reactions is produced either directly or indirectly from products of this free radical decomposition process. It would be expected to abstract a hydrogen atom from C_2H_3Br or some other hydrogen source in the reaction mixture producing $C_2H_4Br_2$. A similar hydrogen abstraction reaction involving the vinyl radical, reaction 5, is proposed as the main source of ethylene.

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br \quad (5)$$

The presence of vinyl acetylene in the reaction products, particularly at the higher temperatures, is consistent with the reaction sequence

$$C_2H_3 + C_2H_2 \rightarrow C_4H_5 \quad (16)$$

$$C_4H_5 \rightarrow C_4H_4 + H \quad (17)$$

This would be most important at the higher temperatures where the yield of C_2H_2 is proportionately the largest and the temperature would be large enough to compensate for the expected comparatively large activation energy of reaction 17. Vinyl acetylene is thus regarded as a secondary product resulting from a reaction involving C_2H_2, the stable primary reaction product formed in the largest concentration.

Summary

We have extended experimental kinetic measurements of the thermal decomposition of vinyl bromide to much lower temperatures than have previously been examined. As the temperature decreases, the extent of decomposition via the molecular elimination of HBr also decreases, making it possible to observe a new, second-order, free radical channel leading to bromine atoms and vinyl radicals. We are unaware of any previous characterization of this free radical channel for the decomposition of vinyl bromide. We have separated the kinetic behavior of the molecular elimination of HBr from this free radical pathway and report estimates of the rate constants for the molecular channel that extrapolate well to the earlier, high-temperature results obtained by quite different experimental methods. Our own experiments over a limited range of low temperatures lead to an activation energy of 220 kJ mol^{-1} for the molecular channel, while a linear Arrhenius representation of both our data and the higher temperature results leads to an activation energy of 250 kJ mol^{-1}. The molecular channel was found to be second order, and its rate constant depended on whether the bath gas was vinyl bromide or argon. We therefore conclude that the molecular channel depends strongly on energy transfer from the bath gas. On the other hand, the rate constants for the formation of products characteristic of the free radical path are second order and independent of the nature of the bath gas. We propose that the generation of vinyl radicals results from disporportionation of vinyl bromide with an activation energy of approximately 150 kJ mol^{-1}, much less than the C−Br energy in vinyl bromide, and reminiscent of the situation that has been shown to occur in the pyrolysis of ethylene at temperatures below 1000 K.

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