Kinetic Modeling Analysis of the Pyrolysis of Vinyl Bromide

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A kinetic model has been developed for the thermal decomposition of vinyl bromide at temperatures below approximately 750 K. The decomposition is initiated by two channels, a pressure dependent molecular channel, $C_2H_3Br + M \rightarrow C_2H_2 + HBr + M$, and a free radical channel, $2\ C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2$. The molecular channel is second-order overall at all the temperatures and pressures investigated. The temperature dependence of the rate constant for this reaction when vinyl bromide is M is given by $\ln(k_{1a}) = 35.7 \pm 5.4 - 29.8 \times 10^3(\pm 12\%)/T$. This leads to a preexponential factor of 3×10^{15} L mol^{-1} s^{-1} and an activation energy of 248 kJ mol^{-1}. When M is argon, the preexponential factor is 2×10^8 L mol^{-1} s^{-1} and the activation energy is 153 kJ mol^{-1} ± 23%. The temperature dependence of the free radical decomposition step is given by $\ln(k_2) = 17.3 \pm 3.2 - (17.3 \times 10^3 \pm 13\%)/T$, giving a preexponential factor of 3×10^7 L mol^{-1} s^{-1} and an activation energy of 144 kJ mol^{-1}. The model also provides kinetic data for the abstraction of hydrogen from vinyl bromide by C_2H_3 radicals, $C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br$. The temperature dependence of this reaction is given by $\ln(k_3) = 28.7 \pm 3.1 - 9.7 \times 10^3(\pm 22\%)/T$, leading to a preexponential factor of 3×10^{12} L mol^{-1} s^{-1} and an activation energy of 81 kJ mol^{-1}.

Introduction

We have recently reported the results of an experimental study of the kinetics of the thermal decomposition of vinyl bromide at temperatures between 647 and 733 K[1]. That study identified two decomposition channels. A molecular decomposition, reaction 1,

$$C_2H_3Br \rightarrow C_2H_2 + HBr \qquad (1)$$

had been reported in earlier experiments at temperatures ranging from about 800 K to 2100 K.[2−5] The only hydrocarbon product identified in that work was C_2H_2 and the reaction was found to be in its falloff region at all the pressures investigated. This has also been confirmed to be the dominant decomposition channel in both infrared multiphoton decomposition work[6] and theoretical treatments of vinyl bromide decomposition.[7,8] It has been postulated that reaction 1 proceeds by formation of vinylidene which then rapidly isomerizes to acetylene but no direct experimental confirmation of this has so far been reported.

The second channel observed in our experimental study led to additional reaction products such as C_2H_4, 1,3-C_4H_6, $C_2H_4Br_2$, and vinyl acetylene, many of which cannot easily be accounted for by reaction 1, even assuming it to proceed through the vinylidene intermediate. The kinetic behavior of these products indicated a second decomposition path involving free radicals and proceeding with both a substantially smaller activation energy and a smaller preexponential factor than reaction 1. The yields of these products relative to acetylene decreased sharply with increasing temperature as a result of this difference in kinetic behavior and it is unlikely that they would have been observable in the higher temperature experiments reported previously. We proposed that, by analogy with the known mechanism of thermal decomposition of ethylene in its lower temperature regime,[9] the new free radical initiation process in the thermal decomposition of vinyl bromide was likely to be

$$2\ C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2 \qquad (2)$$

This suggestion was consistent both with the formation of the additional hydrocarbon products and with their kinetic behavior as a function of pressure and temperature.

The evident production of significant concentrations of C_2H_3 in the pyrolysis of vinyl bromide raises the possibility of its use to study reactions of the C_2H_3 radical. Although such experiments would clearly be indirect sources of kinetic data, they would provide a useful supplement to the currently rather sparse supply of kinetic information on this species. Among the ultimate objectives of such work would be an improved understanding of the fundamental kinetic behavior of this, the prototypical unsaturated hydrocarbon free radical, and a better appreciation of its role in processes such as carbon deposition and soot formation that are of practical importance in hydrocarbon utilization. The scarcity of “clean” sources of significant concentrations of the vinyl radical, combined with the difficulty in making sensitive, nondestructive, and selective direct observations of it in reaction systems, provides an incentive for finding alternative ways of gaining kinetic information on its chemical reactions.

An empirical kinetic analysis such as that provided in our earlier work on the thermal decomposition of vinyl bromide is useful in identifying the nature of the chemical reactions taking place and in providing a general picture of the kinetic behavior of the reactions leading to specific products. In ideal situations, such an analysis can occasionally also provide kinetic information about specific chemical reactions. However, the unequivocal assignment of kinetic parameters to specific chemical reactions hinges on having a detailed reaction mechanism which can be analyzed using the tools available through kinetic modeling. The development of such a mechanism and an evaluation of its range of application is the central objective of the work we report here. This will allow us to evaluate the impact of the assumptions made in our empirical analysis and will provide a more reliable separation of the molecular and free radical decomposition channels. It will also allow us to estimate the kinetic

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parameters of specific reactions, some of which involve the vinyl radical, leading to the products of the free radical decomposition rather than simply evaluating Arrhenius parameters for the overall processes leading to those products.

Experimental Section

The experimental details have been described previously,[1] but are summarized here to provide an experimental context for the kinetic modeling. Most of the experimental results used in developing the kinetic model were reported in our earlier paper but some additional experiments were made, particularly in verifying the range of reaction products under our conditions and evaluating the effect of pressure on the molecular decomposition channel. Relatively low temperatures were required to reduce the importance of the molecular decomposition sufficiently to make the contribution of the free radical decomposition channel significant. Under these conditions, the overall rate of decomposition was quite slow making batch experiments preferable to flow experiments. A reaction mixture of the desired composition and pressure was introduced to a Pyrex reaction vessel and allowed to react for a measured length of time. When the desired time had elapsed, a measured pressure of the reaction mixture was transferred to the sample loop of a gas chromatograph for analysis. The reaction temperature was measured with calibrated iron−constantan thermocouples and the pressures were measured with calibrated piezoelectric pressure transducers. When the time course of the reaction was measured in this way for identical conditions of pressure, temperature and initial composition of the reaction mixture but using reaction vessels with surface-to-volume ratios differing by a factor of 10, the results obtained in the different reaction vessels were indistinguishable.

The gas chromatographic analysis used either a Perkin-Elmer Sigma 3 or a Hewlett-Packard HP5880 gas chromatograph. Hydrocarbon products were determined using a 30 foot, 1/8 in. diameter column packed with 23% SP1700 on Chromosorb P. Brominated products were measured with a 6 foot, 1/8 in. diameter column packed with 0.1% SP1000 on Carbopack C. Both instruments were equipped with a flame ionization detector and the HP5880 was also interfaced to a Ametek Dycor MA-200M quadrupole mass spectrometer. In our earlier work, only the yields of C_2H_2, C_2H_4, and 1,3-C_4H_6 could be measured. Vinyl acetylene, C_4H_4, was well resolved and was identified by its mass spectrum but could not be quantified because we could not obtain authentic material for calibration purposes. Dibromoethane was identified by its mass spectrum. It was well resolved from the other components of the reaction mixture on the SP1000 column but this column did not resolve the hydrocarbon reaction products. We have used the SP1000 column to extend the analytical data obtained in our earlier study to include dibromoethane. The 1,1- and 1,2-dibromo isomers are well resolved on this column and the combination of retention time and mass spectrum identified the $C_2H_4Br_2$ product as the 1,2- isomer. Although HBr is undoubtedly a reaction product, it could not be detected or measured with the available instrumentation.

Vinyl bromide was obtained from the Aldrich Chemical Co. and had a stated purity of 98%. It contained methyl ethyl hydroquinone as an inhibitor and was purified by freeze pump thaw cycles followed by bulb to bulb distillation. The argon used in the experiments to evaluate the pressure dependence of the reaction was obtained from Praxair Products Inc. and had a stated purity of 99.9995%.

The kinetic modeling was done on a personal computer using software which we have used previously.[9] Rate constants were provided as input in Arrhenius form with the activation energies and preexponential factors obtained from literature sources.[10−14] Adjustment of the rate constants for the reactions in the model was guided by sensitivity analysis, microscopic reversibility, and by the estimates of uncertainty in the data obtained from the literature. The number of reactions for which rate constants could be adjusted was limited by the number of reaction products for which measured yields were obtained as well as by the sensitivity of the computed yield of a given product to the numerical value of the rate constant assigned to a specific reaction. Rate constants were adjusted manually until the curves representing the calculated product yields appeared visually to represent the median trend of the experimentally measured yields. The number of experimental data points for composition as a function of reaction time at a given reaction pressure and temperature was generally insufficient to justify the use of a statistical method of either fitting the rate constants for reactions in the model or assessing goodness of fit. Reactions to which the measured concentrations were not sufficiently sensitive to permit this approach were not considered appropriate for use in adjusting the calculated product yields to fit the experimental data. The rate constants that were fitted in this way for each set of reaction conditions were constrained to fit an Arrhenius form of temperature dependence.

Results and Discussion

Development of the Mechanism. Development of a mechanism for analysis starts with the two channels for decomposition of vinyl bromide identified in our earlier work[1]

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

$$2\,C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2 \tag{2}$$

The free radical component of the overall reaction is initiated by reaction 2 and deduction of the important subsequent reactions of the free radicals formed in that step must first consider the reactions of these species with the parent molecule, vinyl bromide. These are

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br \tag{3}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br \tag{4}$$

$$C_2H_3Br_2 + C_2H_3Br \rightarrow C_2H_4Br_2 + C_2H_2Br \tag{5}$$

$$C_2H_3Br_2 + C_2H_3Br \rightarrow C_4H_6Br_3 \tag{6}$$

There is good evidence that decomposition of brominated free radicals by cleavage of the C−Br bond is rapid[15,16] and an activation energy of 27 kJ mol^{-1} has been estimated[16] for the decomposition of C_2H_4Br. Reactions 4 and 6 are expected to produce vibrationally excited products which, especially at low pressures, would be expected to decompose particularly readily. These factors require consideration of the following additional reactions

$$C_2H_2Br \rightarrow C_2H_2 + Br \tag{7}$$

$$C_2H_3Br_2 \rightarrow C_2H_3Br + Br \tag{8}$$

$$C_4H_6Br \rightarrow C_4H_6 + Br \tag{9}$$

$$C_4H_6Br_3 \rightarrow C_4H_6Br_2 + Br \tag{10}$$

The yield of 1,3-C_4H_6 was independent of total pressure from 20 to 80 kPa when the partial pressure of vinyl bromide was kept constant and the total pressure was increased by adding argon. We take this to indicate that, under our experimental conditions, any excess vibrational energy is sufficiently relaxed

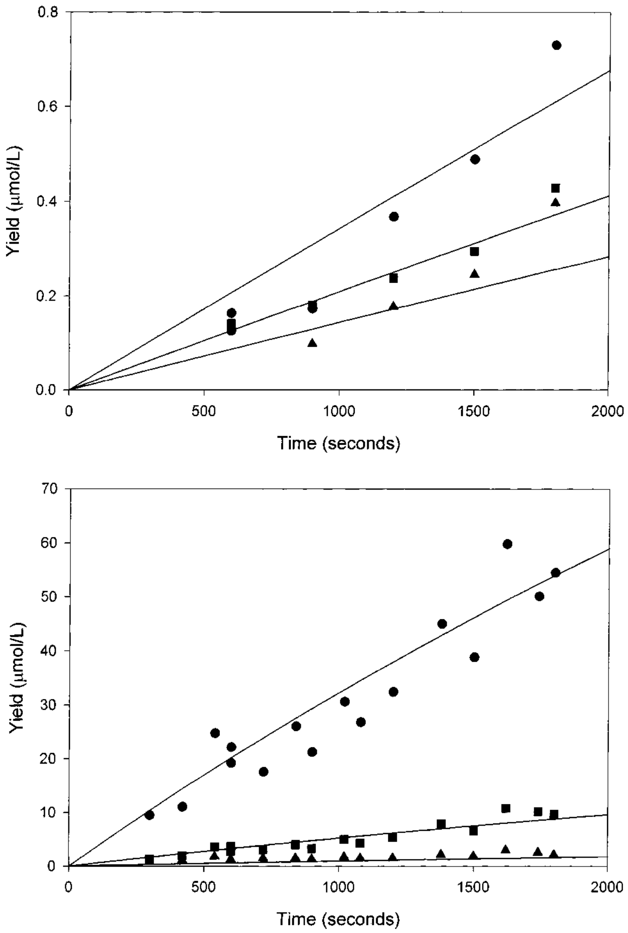

Figure 1. (a) Representative plots of the dependence of product yields on reaction time at 636 K and a total pressure of 16 kPa. The plotting symbols represent the experimental measurements and the lines represent the fit obtained with the kinetic model. ● C_2H_2, ■ C_2H_4, ▲ 1,3-C_4H_6. (b) Representative plots of the dependence of product yields on reaction time at 733 K and a total pressure of 16 kPa. The plotting symbols represent the experimental measurements and the lines represent the fit obtained with the kinetic model. ● C_2H_2, ■ C_2H_4, ▲ 1,3-C_4H_6.

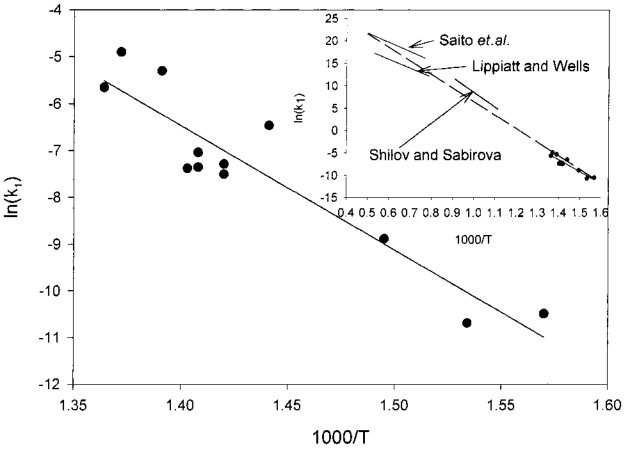

Figure 2. Temperature dependence of the rate constant for 2 $C_2H_3Br \rightarrow C_2H_2 + HBr + C_2H_3Br$.

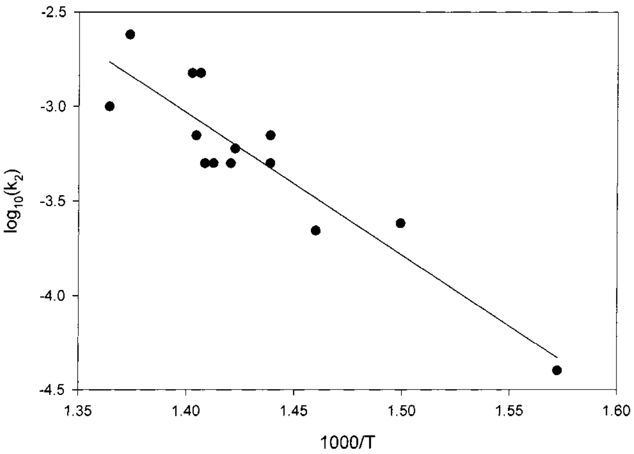

Figure 3. Temperature dependence of the rate constant for 2 $C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2$.

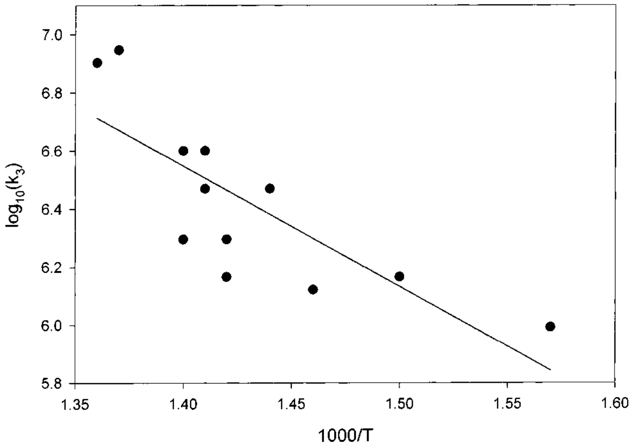

Figure 4. Temperature dependence of the rate constant for $C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br$.

by collisions with the bath gas that it does not measurably affect the product yields. This is consistent with the analysis of the model in Figures 5 and 6 which indicate that reaction 9 has a large flux and a negligible sensitivity coefficient. This leads to the conclusion that, even without considering vibrational excitation, reaction 9 plays a dominant role in producing 1,3-C_4H_6 and is not kinetically limiting for that product. Increasing the value of k_9, as would be done in making allowance for vibrational excitation, would have no effect on the calculated yield of 1,3-C_4H_6 because of this small sensitivity coefficient.

We see no evidence in the chromatograms for products of molecular weight larger than that of $C_2H_4Br_2$. This suggests that the yield of $C_4H_6Br_2$ is small relative to the other products observed or that it is lost in the transfer line to the gas chromatograph or becomes incorporated into deposits on the surface of the reaction vessel and is effectively removed from the sphere of homogeneous chemical reaction. Because reaction 10 represents the decomposition of a brominated free radical and presumably is fairly rapid, as discussed earlier, it follows either that formation of $C_4H_6Br_3$ in reaction 6 is slow or that this radical or its reaction products are lost on the walls of the glass vacuum system or that its precursor, $C_2H_3Br_2$, has loss routes that compete efficiently with its addition to vinyl bromide in reaction 6. These are features of the reaction which a satisfactory model must seek to resolve.

In our earlier empirical analysis of this reaction, we attributed the formation of C_2H_4 to reaction 3 and assumed that the C_2H_2-Br radical formed in this process would decompose rapidly via reaction 7 giving a yield of C_2H_2 from the free radical decomposition channel equivalent to the yield of C_2H_4. Similarly, the measured yield of 1,3-C_4H_6 was attributed to reaction 4 followed by reaction 9. The efficient production of atomic bromine in reactions 7 through 10 requires an analysis of the impact of the subsequent reactions of Br on the yields of the

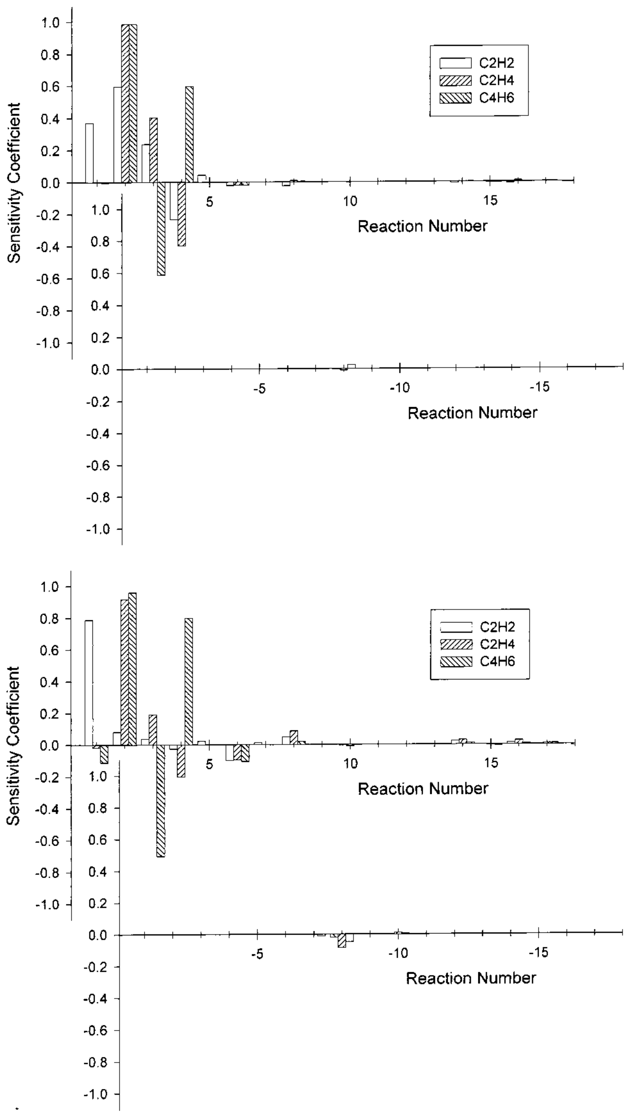

Figure 5. (a) Sensitivity coefficients for reactions in the model at 636 K. Vinyl bromide pressure = 16 kPa, reaction time = 2000 s. (b) Sensitivity coefficients for reactions in the model at 733 K. Vinyl bromide pressure = 16 kPa, reaction time = 2000 s.

hydrocarbon products. In contrast to atomic chlorine and fluorine, Br atoms do not abstract hydrogen readily from hydrocarbons. However, the addition of Br to alkenes and alkynes occurs much more readily than abstraction[17] and the following reaction requires evaluation, as well as the reverse of reactions 7 through 10 above.

$$C_2H_4 + Br \rightarrow C_2H_4Br \tag{11}$$

Of these, it is anticipated that reaction −8 will be the most important because the concentration of vinyl bromide is more than a factor of 100 larger than the concentrations of acetylene, ethylene, or butadiene.

We have observed 1,2-$C_2H_4Br_2$ in the present work using gas chromatography. The $C_2H_4Br_2$ was identified as the 1,2-isomer by comparing its retention time with that of an authentic sample. The peaks due to 1,1-$C_2H_4Br_2$ and 1,2-$C_2H_4Br_2$ are well separated with retention times of 10 min and 17 min, respectively on the SP1000 column under the chromatographic conditions used in our experiments (6’ × 1/8” SP1000 on Carbopak C, He at 40 mL/minute, isothermal at 90 °C). This means that reaction 5 provides a source of C_2H_2Br, and therefore ultimately of C_2H_2, that was overlooked in interpreting our earlier measurements. Consequently, the estimates of the rate

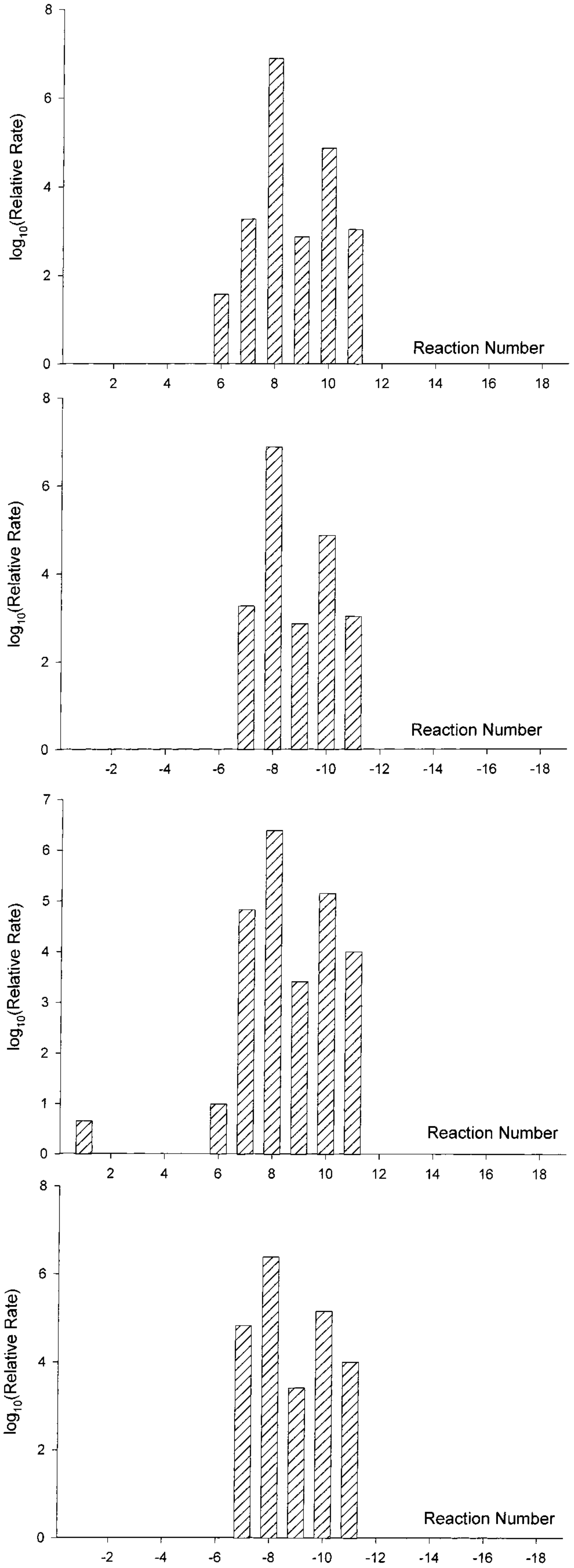

Figure 6. (a) Calculated reaction rates at 636 K relative to reaction 2. Vinyl bromide pressure = 16 kPa, reaction time = 2000 s.(b) Calculated reaction rates at 733 K relative to reaction 2. Vinyl bromide pressure = 16 kPa, reaction time = 2000 s.

constants for the molecular decomposition channel, reaction 1, in our earlier work are actually upper limits and must be reduced to the extent required to compensate for the additional C_2H_2 that is a consequence of the formation of $C_2H_4Br_2$ and C_2H_2Br in reaction 5. Because both the addition of Br to π bonds and the decomposition of brominated free radicals are rapid, such reactions are likely to be nearly equilibrated. The concentration of vinyl bromide is so much larger than the concentrations of C_2H_2, C_2H_4 and 1,3-C_4H_6 that reactions 8 and −8 are expected to control the concentrations of both Br and $C_2H_3Br_2$, the immediate precursor to 1,2-$C_2H_4Br_2$. The observation of a measurable yield of this compound suggests that reaction 8 allows appreciable concentrations of $C_2H_3Br_2$ to exist under our reaction conditions.

The most important termination reactions should be those involving the radicals formed in reaction 2. Because it is indicated that atomic bromine is formed in several radical decomposition processes, their recombination should also be included at this stage

$$2\ C_2H_3 \rightarrow C_4H_6 \tag{12}$$

$$2\ C_2H_3Br_2 \rightarrow C_4H_6Br_4 \tag{13}$$

$$2\ Br + M \rightarrow Br_2 + M \tag{14}$$

$$Br + C_2H_3 \rightarrow C_2H_2 + HBr \tag{15}$$

$$Br + C_2H_3Br_2 \rightarrow C_2H_2Br_2 + HBr \tag{16}$$

In reaction 14, M is any third body but will be taken to be C_2H_3Br in the experiments using pure vinyl bromide because of the small (less than a few percent) extent of reaction examined in those experiments. Most of these termination reactions do not have easily observable signatures. There are sources of butadiene such as reaction 9 that could compete effectively with reaction 12 making it impossible to identify the observed butadiene yields unequivocally with reaction 12. We were unable to find chromatographic evidence for any products of molecular weight as large as that of $C_4H_6Br_4$. However, this could be due to the low volatility of $C_4H_6Br_4$ making it uncertain whether reaction 13 occurs to a significant extent. Because the $C_2H_3Br_2$ radical evidently produces 1,2-$C_2H_4Br_2$ in reaction 5, both this and the addition of $C_2H_3Br_2$ to vinyl bromide (reaction 6) may be able to compete effectively with reaction 13 as a loss route for $C_2H_3Br_2$. The Br_2 formed in reaction 14 would be expected to react significantly with the free radicals present in the system making measurement of its yield of little value in assessing the importance of reaction 14.

The cross reactions of atomic bromine with organic free radicals evidently differ from the simple combination reactions that one might expect. The NIST Chemical Kinetics Database[14] lists reactions 15 and 16 but makes no reference to the simple combination reactions that would give C_2H_3Br and $C_2H_3Br_3$, respectively, presumably because these adducts are likely contain sufficient energy to decompose rapidly to the products listed in reactions 15 and 16. In the case of C_2H_3Br, calculations on a vinyl bromide potential energy surface[7,8] indicate that decomposition by elimination of HBr will dominate oversimple C−Br bond cleavage and the decomposition of $C_2H_3Br_3$ presumably occurs in a similar manner so reactions 15 and 16 should be regarded as a composite of two elementary processes. Reaction 15 would increase the yield of C_2H_2 if it occurred to a significant extent. Although this can be tested by kinetic modeling, the reaction does not have a unique signature that would permit experimental evaluation of its importance. If reaction 16 were to occur to a significant extent, one would expect to see $C_2H_2Br_2$ among the reaction products. The absence of $C_2H_2Br_2$ in the chromatograms suggests that reaction 16 is not important under our conditions. Fortunately, the rate constants for these termination reactions can be estimated with sufficient reliability to assess their importance through kinetic modeling calculations.

The set of reactions suggested in our earlier work as a framework within which to understand the early stages of pyrolysis of vinyl bromide is listed below, together with initial estimates of the Arrhenius parameters for these reactions. We have added reactions 5, 6, and 10 to these on the basis of the preceding discussion. The parameters for reactions 1a and 2

$$C_2H_3Br + M \rightarrow C_2H_2 + HBr + M$$
$$[A = 8.2 \times 10^{15}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 250\ \mathrm{kJ\ mol^{-1}}] \tag{1a}$$

$$2\ C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2$$
$$[A = 8.0 \times 10^{6}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 150\ \mathrm{kJ\ mol^{-1}}] \tag{2}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br$$
$$[A = 5.83 \times 10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 121\ \mathrm{kJ\ mol^{-1}}] \tag{3}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br$$
$$[A = 2 \times 10^{8}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 30\ \mathrm{kJ\ mol^{-1}}] \tag{4}$$

$$C_2H_3Br_2 + C_2H_3Br \rightarrow C_2H_4Br_2 + C_2H_2Br$$
$$[A = 5.83 \times 10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 121\ \mathrm{kJ\ mol^{-1}}] \tag{5}$$

$$C_2H_3Br_2 + C_2H_3Br \rightarrow C_4H_6Br_3$$
$$[A = 2 \times 10^{8}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 30\ \mathrm{kJ\ mol^{-1}}] \tag{6}$$

$$C_2H_2Br \rightarrow C_2H_2 + Br$$
$$[A = 6.81 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 27\ \mathrm{kJ\ mol^{-1}}] \tag{7}$$

$$C_2H_3Br_2 \rightarrow C_2H_3Br + Br$$
$$[A = 6.81 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 27\ \mathrm{kJ\ mol^{-1}}] \tag{8}$$

$$C_2H_3Br + Br \rightarrow C_2H_3Br_2$$
$$[A = 3.16 \times 10^{9}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 12\ \mathrm{kJ\ mol^{-1}}] \tag{−8}$$

$$C_4H_6Br \rightarrow C_4H_6 + Br$$
$$[A = 6.81 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 27\ \mathrm{kJ\ mol^{-1}}] \tag{9}$$

$$C_4H_6Br_3 \rightarrow C_4H_6Br_2 + Br$$
$$[A = 6.81 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}},\ E_a = 27\ \mathrm{kJ\ mol^{-1}}] \tag{10}$$

were taken from our earlier work.[1] The rate constants for addition of free radicals to vinyl bromide were assumed to be comparable to those for addition of C_2H_5 to ethylene[14] and the rate constants for reactions 3 and 5 were assumed to be comparable to that for abstraction of hydrogen from ethylene by C_2H_5.[18] The kinetic parameters for the decompositions of the brominated free radicals were assumed to be comparable to those estimated for decomposition of C_2H_4Br[16] and the rate constant for addition of Br to vinyl bromide was assumed to be comparable to that for addition of Br to C_2H_4.[10] Although no termination steps have been included, this simple series of reactions gives calculated yields of C_2H_2 that are of the correct magnitude and yields of C_2H_4 and 1,3-C_4H_6 that are smaller than the measured yields but not unreasonably so given the approximations employed. What was immediately clear was that the calculated Br atom concentration was orders of magnitude larger than the concentration of any other radical, indicating that reaction 14 is obviously important.

$$2\ \mathrm{Br} + \mathrm{M} \rightarrow \mathrm{Br}_2 + \mathrm{M} \qquad (14)$$

The kinetic parameters for this reaction are known with good accuracy[19] and its inclusion reduced the calculated Br atom concentration to a reasonable magnitude and improved the agreement between the calculated and experimental yields of C_2H_2.

Because recombination of atomic bromine produces significant concentrations of Br_2, the reactions of the free radicals in this system with Br_2 now required evaluation. The radicals calculated to be present in the largest concentrations were $C_2H_3Br_2$ and C_2H_3. The reactions of a number of free radicals, including C_2H_3, with Br_2 have been studied[20] and the following reactions were inserted at this stage, each with the same kinetic parameters.

$$\mathrm{C_2H_3Br_2} + \mathrm{Br_2} \rightarrow \mathrm{C_2H_3Br_3} + \mathrm{Br} \qquad (17)$$

$$\mathrm{C_2H_3} + \mathrm{Br_2} \rightarrow \mathrm{C_2H_3Br} + \mathrm{Br} \qquad (18)$$

Neither reaction had an effect on the calculated yields of the measured products. Reaction 17 led to a calculated yield of $C_2H_3Br_3$ that was comparable to those of C_2H_4 or 1,3-C_4H_6. Although we were not able to detect $C_2H_3Br_3$ among the reaction products, the isomers of this compound have boiling points of nearly 200 °C and might well have too low volatility to pass through the transfer lines to the gas chromatograph. Reaction 18 is not directly observable because it regenerates the starting material, vinyl bromide. On the other hand, its occurrence to a significant extent would have a noticeable effect on the calculated yields of products such as C_2H_4 that are attributable to the C_2H_3 radical. The absence of such effects indicates that reaction 18 does not have a significant influence on the yields of the measured products and similar results were obtained on testing the reactions with Br_2 of the other free radicals in the system, calculated to be present at even smaller concentrations.

In our earlier work, we discussed the possible occurrence of reaction 19.

$$\mathrm{Br} + \mathrm{C_2H_3Br} \rightarrow \mathrm{HBr} + \mathrm{C_2H_2Br} \qquad (19)$$

The involvement of this reaction to a significant extent would provide an additional source of C_2H_2 via the rapid decomposition of C_2H_2Br

$$\mathrm{C_2H_2Br} \rightarrow \mathrm{C_2H_2} + \mathrm{Br} \qquad (7)$$

We concluded that reaction 19 was unlikely to provide an important additional source of C_2H_2 because the addition of Br to vinyl bromide, reaction −8, was likely to have a substantially larger rate constant. Alternatively, reaction −8 could be viewed as producing an adduct, $C_2H_3Br_2$, that could decompose by two channels in the following way

$$\mathrm{Br} + \mathrm{C_2H_3Br} \rightarrow \mathrm{C_2H_3Br_2} \qquad (-8)$$

$$\mathrm{C_2H_3Br_2} \rightarrow \mathrm{C_2H_2Br} + \mathrm{HBr}$$

$$\mathrm{C_2H_3Br_2} \rightarrow \mathrm{C_2H_3Br} + \mathrm{Br} \qquad (8)$$

Reaction 19 would then be a composite of the first two reactions above. The adduct might be expected to possess excess vibrational energy and this would enhance both of its decomposition channels although it might be expected that the rate of reaction 8 would be increased to a greater extent because the newly formed C−Br bond would initially contain most of the excess energy.

TABLE 1: Reactions and Kinetic Parameters Used in the Mechanism for the Pyrolysis of Vinyl Bromide

reaction	A	E_a	reference
(1a) $2\ C_2H_3Br \rightarrow C_2H_2 + HBr + C_2H_3Br$	3×10^{15}	248	this work
(1b) $C_2H_3Br + Ar \rightarrow C_2H_2 + HBr + Ar$	2×10^{8}	153	this work
(2) $2\ C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2$	3×10^{7}	144	this work
(3) $C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br$	3×10^{12}	81	this work
(4) $C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br$	2×10^{8}	30	estimate
(5) $C_2H_3Br_2 + C_2H_3Br \rightarrow C_2H_4Br_2 + C_2H_2Br$	5.83×10^{11}	121	estimate
(6) $C_2H_3Br_2 + C_2H_3Br \rightarrow C_4H_6Br_3$	2×10^{8}	30	estimate
(7) $C_2H_2Br \rightarrow C_2H_2 + Br$	6.81×10^{10}	27	estimate
(8) $C_2H_3Br_2 \rightarrow C_2H_3Br + Br$	6.81×10^{10}	27	estimate
(−8) $C_2H_3Br + Br \rightarrow C_2H_3Br_2$	3.16×10^{9}	12	estimate
(9) $C_4H_6Br \rightarrow C_4H_6 + Br$	6.81×10^{10}	27	estimate
(10) $C_4H_6Br_3 \rightarrow C_4H_6Br_2 + Br$	6.81×10^{10}	27	estimate
(11) $C_2H_4 + Br \rightarrow C_2H_4Br$	3.16×10^{9}	12	estimate
(−11) $C_2H_4Br \rightarrow C_2H_4 + Br$	6.81×10^{10}	27	estimate
(14) $2\ Br + M \rightarrow Br_2 + M$	1.10×10^{9}	−9.23	19
(16) $Br + C_2H_3Br_2 \rightarrow C_2H_2Br_2 + HBr$	7.00×10^{9}	0	estimate
(17) $C_2H_3Br_2 + Br_2 \rightarrow C_2H_3Br_3 + Br$	2.40×10^{10}	−2.4	estimate
(18) $C_2H_3 + Br_2 \rightarrow C_2H_3Br + Br$	2.40×10^{10}	−2.4	20

Kinetic parameters are given in Arrhenius form with the preexponential factor (A) in the units liters, moles, and seconds as appropriate to the reaction order. Activation energies (E_a) are given in kJ mol^{-1}. The rationale for the estimated parameters is discussed in the text.

Unfortunately, reaction 19 does not have a unique signature that would permit its effect to be isolated experimentally. Kinetic experiments on the reaction of Br with ethylene have consistently demonstrated that hydrogen abstraction by Br is too slow to detect relative to its addition[17,21−23] and a recent study of the reaction of Br with propene[15] concluded that the reaction occurred by only two channels; addition to the double bond and hydrogen abstraction from the methyl substituent. If reaction 19 were to occur to a significant extent, it would combine with reaction 7 to produce a catalytic chain converting C_2H_3Br to C_2H_2 and HBr and regenerating atomic Br. The model is consistent with the experimental data on olefins, predicting that unless the rate constant k_{19} is several orders of magnitude smaller than k_{-8} this chain would produce yields of C_2H_2 that are many times larger than we observe, relative to C_2H_4 and 1,3-C_4H_6, and would produce nearly complete consumption of vinyl bromide on a time scale much shorter than that used in our experiments. The observation that the consumption of vinyl bromide in our experiments was at most a few percent and that the yields of C_2H_2 were of roughly the same order of magnitude as those of C_2H_4 and 1,3-C_4H_6 suggests that our conclusion is reasonable that k_{19} is too small to make this reaction significant and is consistent with information in the literature on the reactions of atomic bromine with olefins. As with the earlier discussion of the possible impact of vibrational excitation of C_4H_6Br on its decomposition to C_4H_6, reference to Figures 5 and 6 indicates that the fluxes of reactions 8 and −8 are large and nearly equal while the sensitivity coefficients for these reactions are very small. The consequence of this small sensitivity coefficient is that an increase in the value of k_8, as would be required to allow for vibrational excitation, would have virtually no effect on the concentration of $C_2H_3Br_2$ or its decomposition products.

The reactions identified at this point as being important in describing the product yields in the pyrolysis of pure vinyl bromide provide a sufficient model for fitting the observed yields of C_2H_2, C_2H_4, and 1,3-C_4H_6 over the full temperature range at a pressure of 16 kPa. These reactions are presented in Table 1 together with their Arrhenius parameters. On the assumption that the yields of C_2H_4 and 1,3-C_4H_6 are kinetically limited by the rate of reaction 2, the value of k_2 was adjusted to provide agreement with the total measured yields of these products. If it is further assumed that the decomposition of brominated free radicals (e.g., reactions 7 and 9) is rapid,[16,17] the ratio of yields of C_2H_4 and 1,3-C_4H_6 is controlled by the ratio of the rate constants of reactions 3 and 4. Reaction 3 is a hydrogen abstraction and is therefore likely to have a significantly larger activation energy than reaction 4 which is a free radical addition. Because reactions 2, 3, and 4 all affect the yields of the two products, C_2H_4 and 1,3-C_4H_6, it is only possible to adjust the values of the rate constants of two of these reactions. The value of k_2 was chosen for adjustment of the sum of C_2H_4 and 1,3-C_4H_6. We then adjusted the value of k_3 to provide agreement with the ratio of the yields of these products on the basis that this rate constant should show a greater sensitivity to temperature than k_4. We have kept the Arrhenius parameters for reaction 4 as initially estimated. This means that the accuracy of our activation energy and preexponential factor for reaction 3 are directly dependent on the accuracy of the parameters used for reaction 4.

We have now obtained data for the yields of $C_2H_4Br_2$. These were approximately an order of magnitude smaller than the yields of ethylene and 1,3-butadiene and could not be measured with sufficient accuracy or precision to justify their use in adjusting the rate constant for reaction 5. However, the yields of $C_2H_4Br_2$ were consistent with a preexponential factor of roughly 10^{12} L mol^{-1} s^{-1} and an activation energy of about 110 kJ mol^{-1} for reaction 5, which are comparable to the values, 5.83×10^{11} L mol^{-1} s^{-1} and 121 kJ mol^{-1}, reported recently for the abstraction of hydrogen from ethylene by ethyl radicals.[18] The value of the preexponential factor is unlikely to be substantially larger than 10^{12} L mol^{-1} s^{-1} and the use of a smaller value of the preexponential factor would require a smaller value of the activation energy. The magnitude of these estimates of the Arrhenius parameters for reaction 5 is roughly the same as those deduced here for reaction 3. However, use in reaction 5 of the Arrhenius parameters calculated for reaction 3 seriously overestimated the yields of $C_2H_4Br_2$. The yield of $C_2H_4Br_2$ depends on the relative rates of reactions 5 and 6. We believe that the rate constant of the hydrogen abstraction process (reaction 5) will control the temperature dependence of the yield of $C_2H_4Br_2$ because its activation energy is likely to be significantly larger than that of reaction 6. These results suggest that the activation energy for reaction 5 is significantly larger than that of reaction 3. Increasing or decreasing the value of k_5 in the model did not produce a change in the calculated yields of C_2H_2, C_2H_4 or 1,3-C_4H_6 that would have been measurable in our experiments.

Validation of the Mechanism. Although the model presented at this stage provides a sufficient framework within which to describe the pyrolysis of vinyl bromide at a pressure of 16 kPa over the temperature range 636 K to 733 K, the model requires validation by examining the effects of reverse reactions that have been omitted and of other reactions that were thought to be unimportant. This will provide a reference point at the low end of the range of pressures used in the experiments. We will then examine the application of the model to our experiments at higher pressures, both in pure vinyl bromide and in its mixtures with argon.

As a first step in validation of the mechanism, all the missing reverse reactions for the model presented in Table 1 were added. Kinetic parameters were selected following the principles described in the *Experimental* section. Insertion of these reverse reactions had no effect on the calculated yields of the measured reaction products for a pressure of 16 kPa at both the upper and the lower extremes of the temperature range covered by our experiments. We conclude on this basis that the reverse reactions are not important to the yields of the measured reaction products in our experiments at a pressure of 16 kPa.

All the combination and cross combination reactions of the free radical intermediates were next included. Of these, only reactions 14 and 16 had rates that were significant relative to the free radical initiation process, reaction 2. This is as one would expect

$$2\,Br + M \rightarrow Br_2 + M \qquad (14)$$

$$Br + C_2H_3Br_2 \rightarrow C_2H_2Br_2 + HBr \qquad (16)$$

because the concentrations of Br and $C_2H_3Br_2$ are calculated to be the largest of any radical species in the model. The important effect of reaction 14 was discussed earlier. Although inclusion of reaction 16 produced a significant yield of $C_2H_2Br_2$ in the calculations it had no effect on the calculated yields of the measured products, C_2H_2, C_2H_4, and 1,3-C_4H_6. This is a result of the presence of other sinks for $C_2H_3Br_2$, particularly reaction 8 but also reactions 6 and 17, whose calculated rates are greater than or comparable to that of reaction 16. The occurrence of reaction 16 therefore has no appreciable effect on the rates of formation of the products that result from these more rapid reactions of $C_2H_3Br_2$. As was discussed earlier for reaction 19 between Br and C_2H_3Br, reaction 16 might be better viewed as a composite of

$$Br + C_2H_3Br_2 \rightarrow C_2H_3Br_3$$

$$C_2H_3Br_3 \rightarrow C_2H_2Br_2 + HBr$$

This adduct decomposition to HBr would be in competition with the reverse of the addition step

$$C_2H_3Br_3 \rightarrow C_2H_3Br_2 + Br$$

The adduct would be formed with excess vibrational energy and, as was the case in reaction 19, the latter process might predominate so that the use of only the composite, reaction 16, would overestimate the yield of $C_2H_2Br_2$. Our failure to detect $C_2H_2Br_2$ among the reaction products suggests that the value of k_{16} used in the calculations may be too large or that the rate constants for one or more of the other loss routes for $C_2H_3Br_2$ may be too small, resulting in a calculated concentration of this radical that is too large. However, the insensitivity of the calculated yields of the measured products to the value of k_{16} indicates that our original estimate of the value of this rate constant is adequate for the current purposes and makes it unlikely that the extra detail provided by the chemistry associated with the $C_2H_3Br_3$ species would provide additional useful information.

The observation that the calculated concentration of atomic bromine is by far the largest of any free radical intermediate in this system requires evaluation of the importance of its reactions with the products of the reaction. These are reactions −7, −9, and 11

$$C_2H_2 + Br \rightarrow C_2H_2Br \qquad (-7)$$

$$C_4H_6 + Br \rightarrow C_4H_6Br \qquad (-9)$$

$$C_2H_4 + Br \rightarrow C_2H_4Br \qquad (11)$$

As anticipated earlier, the rates of these reactions were calculated to be much smaller than that of the addition of atomic bromine to vinyl bromide, reaction −8. Moreover, the rate constants of reactions 7, 9, and −11 are large with the result that reactions 7, 9, and 11 are effectively equilibrated. The other potential loss routes for C_2H_2Br, C_2H_4Br, and C_4H_6Br have rate constants that are much too small to allow them to compete with reactions 7, 9, and −11. As a result, inclusion in the model of the addition of Br to C_2H_2, C_2H_4, and 1,3-C_4H_6 had no effect on the yields of the measured reaction products.

Figure 1 indicates the degree of agreement between the model calculations and experiment provided by the model at the upper and lower extremes of temperature at a pressure of 16 kPa. The rate constants for reactions 1, 2, and 3 were adjusted in fitting the model results to the experimental data and the rate constants obtained in this way were consistent with an Arrhenius temperature dependence giving preexponential factors and activation energies, found in Table 1, whose magnitudes were comparable to those reported in the literature for similar reactions. These Arrhenius plots are presented in Figures 2 through 4.

The sensitivity of the calculated yields of the measured reaction products to the rate constants of the reactions in the mechanism is indicated in Figure 5 and the calculated rates of the reactions in the model relative to the free radical initiation process, reaction 2, are indicated in Figure 6. The sensitivity coefficients were calculated by determining the changes in calculated species concentrations produced by systematically changing the rate constants for individual reactions by 1%. Changes of this magnitude are unlikely to significantly change the relative importance of the reactions in the mechanism and are small enough to be within the accuracy limits of the equilibrium constants required for consistency with microscopic reversibility. These results are given for a pressure of 16 kPa of vinyl bromide at the upper and lower ends of the temperature range covered by our experiments. The reaction rates cover a very wide range of values and are therefore plotted on a logarithmic scale. Even so, it is clear that at both ends of the temperature range reactions 7, 8, 9, 10, and 11 have by far the largest rates in both directions and reaction 6 has a substantial rate in the forward direction. At the upper end of the temperature range, the rate of reaction 1 has increased to such an extent that its rate is comparable with that of reaction 6. These reactions are reproduced below for convenience

$$C_2H_3Br_2 + C_2H_3Br \rightarrow C_4H_6Br_3 \tag{6}$$

$$C_2H_2Br \leftrightarrows C_2H_2 + Br \tag{7}$$

$$C_2H_3Br_2 \leftrightarrows C_2H_3Br + Br \tag{8}$$

$$C_4H_6Br \leftrightarrows C_4H_6 + Br \tag{9}$$

$$C_4H_6Br_3 \leftrightarrows C_4H_6Br_2 + Br \tag{10}$$

$$C_2H_4 + Br \leftrightarrows C_2H_4Br \tag{11}$$

The reverse of reaction 6 is unimportant because the decomposition of $C_4H_6Br_3$ is dominated in the model by reaction 10. The sensitivity coefficients in Figure 5 indicate that the yields of the measured products are insensitive to the value of the rate constants for most of these reactions, except for a very small sensitivity to reactions 6, ±8, and ±10. The magnitude of these sensitivity coefficients suggests that changing the value of the rate constant of any of these reactions by a factor of 10 would produce at most a 20% change in the concentration of any of the measured products at the upper end of the temperature range and only a 1% or less change at the lower end of the temperature range. These results confirm that reactions 7 through 11 are virtually equilibrated. Although the yields of the measured products are not sensitive to reaction 11, it and its reverse are included in the mechanism presented in Table 1 because their reaction rates are large.

The sensitivity coefficients in Figure 5 provide some validation of the procedure chosen for selecting the reactions whose rate constants were adjusted in fitting the model calculations to the experimental results. Only reactions 1 through 4 have a sensitive effect on the yields of the measured reaction products. In no case does a reaction have a sensitivity coefficient greater than unity for these products, suggesting that they are not produced in the model to any important extent by catalytic chains. These reactions are reproduced below for convenience

$$2\ C_2H_3Br \rightarrow C_2H_2 + HBr + C_2H_3Br \tag{1a}$$

$$2\ C_2H_3Br \rightarrow C_2H_3 + C_2H_3Br_2 \tag{2}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_2H_4 + C_2H_2Br \tag{3}$$

$$C_2H_3 + C_2H_3Br \rightarrow C_4H_6Br \tag{4}$$

Comparison with the analysis of relative reaction rates leads to the conclusion that the model cleanly separates the kinetic behavior of brominated radicals and atomic bromine, whose important reactions are approximately equilibrated, from the reactions responsible for the decomposition of vinyl bromide and those consuming vinyl radicals all of which exert a degree of kinetic control over the yields of the measured reaction products.

Reaction 1 has a high, selective and positive sensitivity for the C_2H_2 yield at the upper end of the temperature range and only a small negative sensitivity for C_2H_4 and 1,3-C_4H_6. As the temperature decreases, reaction 1 has a less sensitive effect on the yield of C_2H_2 and the sensitivity of the C_2H_2 yield to reactions 2, 3, and 4 increases. However, the positive sensitivity of C_2H_2 to reaction 3 is balanced almost exactly by the negative sensitivity of the C_2H_2 yield to reaction 4. The result is that the yield of C_2H_2 is controlled by both reactions 1 and 2, with the effect of (1) steadily decreasing and that of (2) steadily increasing as the temperature decreases. This makes it critical to fit the rate constant of reaction 2 accurately, particularly at the lower temperatures, before the rate constant of reaction 1 is used to fit the C_2H_2 yield.

Reaction 2 has nearly unit sensitivity for both C_2H_4 and 1,3-C_4H_6 over the full temperature range. Reactions 3 and 4 have compensating sensitivities for C_2H_2, C_2H_4 and 1,3-C_4H_6 so the rate constant of reaction 2 can be used to fit the sum of the yields of C_2H_4 and 1,3-C_4H_6 independently from the yield of C_2H_2. Reaction 3 has a positive sensitivity for the yield of C_2H_4 and a negative sensitivity for the yield of 1,3-C_4H_6, whereas reaction 4 shows the opposite behavior. Because the kinetic effects of these reactions are coupled, neither can be used to independently fit the yields of C_2H_4 and 1,3-C_4H_6. No reaction in the system has both a selective and sensitive effect on the yields of these products, so the best that can be done is to fix the kinetic parameters for one of these reactions and adjust the rate constant for the other one to provide a fit to the ratio of the experimental yields of C_2H_4 and 1,3-C_4H_6. As discussed earlier, we chose to fix the kinetic parameters of reaction 4, which should have the lower activation energy, and adjust the rate constant of reaction 3 to provide agreement with the experimentally measured ratio of yields of C_2H_4 and 1,3-C_4H_6.

The Arrhenius expressions obtained by fitting the rate constants for reactions 1 through 3 may now be compared with the empirical relations reported in our earlier work and with other relevant measurements in the literature. In our earlier work, the value of k_1 was estimated by assuming that all the C_2H_2 produced via free radical sources resulted from decomposition of the C_2H_2Br radical formed in reaction 3. The yield of C_2H_2 from reaction 1 was then estimated as the difference between the measured C_2H_2 and the yield of C_2H_4. The use of a kinetic model in this work makes allowance for additional sources of C_2H_2 such as the production of C_2H_2Br in reaction 5. Consequently, the values of k_1 obtained here are somewhat lower than those obtained in our earlier work, the effect being greater at lower temperatures than at higher ones. This leads to a steeper Arrhenius plot with an activation energy, 248 kJ mol^{-1}, that is larger than the value of 220 kJ mol^{-1} based on our earlier empirical analysis and corresponds almost exactly with the value of 250 kJ mol^{-1} calculated by combining the results of our earlier empirical analysis with the results of high-temperature experiments reported in the literature. The preexponential factor for reaction 1 obtained in the current analysis based on kinetic modeling, 3×10^{15} L mol^{-1} s^{-1}, is much larger than the value of 2.5×10^{13} L mol^{-1} s^{-1} based on our earlier empirical analysis but corresponds reasonably well with the value of 8.2×10^{15} L mol^{-1} s^{-1} based on the combination of our earlier empirical analysis with the high-temperature results in the literature. We also note the wide range of Arrhenius parameters reported in the higher temperature experiments in the literature: ($A = 1.0 \times 10^{17}$ L mol^{-1} s^{-1}, $E_a = 274$ kJ mol^{-1})[2], ($A = 1.0 \times 10^{12}$ L mol^{-1} s^{-1}, $E_a = 163$ kJ mol^{-1})[4] and ($A = 9.5 \times 10^{13}$ L mol^{-1} s^{-1}, $E_a = 170$ kJ mol^{-1}).[5] It is clear from the insert in Figure 2 that our experiments and the three sets of experiments at higher temperatures each span approximately the same extent of $1/T$ although our experiments certainly cover a smaller range of T than the toluene jet or shock tube experiments. The diverse values of the preexponential factor obtained in these experiments illustrate the sensitivity of the value of the Arrhenius preexponential factor to the value of the activation energy determined from experiments over a limited range of temperatures. The quality of the extrapolation of our values of k_1 through the results obtained in the three high-temperature studies gives us some confidence in the accuracy of our representation of the temperature dependence of the rate constant for reaction 1 in pure vinyl bromide.

The activation energy of 144 kJ mol^{-1} calculated for reaction 2 agrees within the experimental uncertainty with the activation energy of 150 kJ mol^{-1} estimated in our earlier work for total C_2H_4 production. This is as expected if reaction 2 is kinetically limiting for C_2H_4. It also agrees within experimental uncertainty with the activation energy for production of 1,3-C_4H_6 calculated in our earlier work, again consistent with reaction 2 being kinetically limiting for 1,3-C_4H_6. In our earlier empirical kinetic analysis, we found an activation energy of 46 kJ mol^{-1} for the ratio of rates of C_2H_4 production to 1,3-C_4H_6 production. The mechanism presented here suggests that this should represent the difference in activation energy of reactions 3 and 4. We measure an activation energy of 81 kJ mol^{-1} for reaction 3 in the current work and assume an activation energy of 30 kJ mol^{-1} for reaction 4, giving a difference of 51 kJ mol^{-1}, again in good agreement with the results of the empirical analysis.

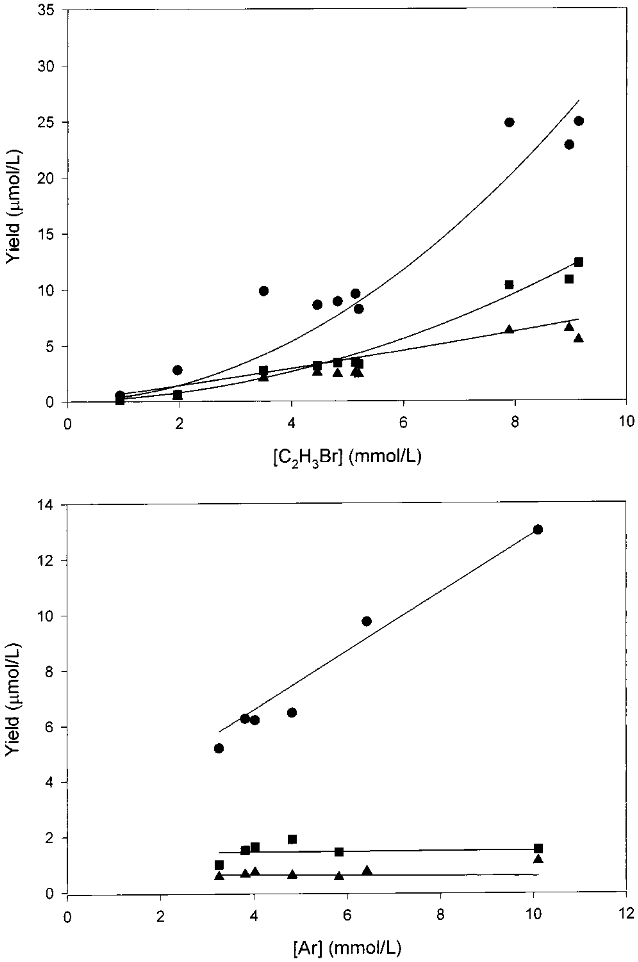

Figure 7. (a) Representative plots of the dependence of product yields on pressure at 705 K and a reaction time of 10 min in pure C_2H_3Br. The plotting symbols represent the experimental measurements and the lines represent the fit obtained with the kinetic model. ● C_2H_2, ■ C_2H_4, ▲ 1,3-C_4H_6. (b) Representative plots of the dependence of product yields on argon pressure at 700 K and a reaction time of 10 min with 16 kPa partial pressure of C_2H_3Br. The plotting symbols represent the experimental measurements and the lines represent the fit obtained with the kinetic model. ● C_2H_2, ■ C_2H_4, ▲ 1,3-C_4H_6.

When the model was applied to kinetic data in which the product yields were measured as a function of vinyl bromide pressure at a fixed reaction time over the same temperature range, the experimental yields of the measured reaction products were reproduced well at pressures of approximately 5 to 50 kPa as indicated in the results presented in Figure 7(a) at 705 K. As the pressure increases, the yields of C_2H_2 and HBr also increase significantly and because these products have by far the largest yields, their potential reactions with other free radicals in the system must be evaluated.

The only reaction that might be expected to occur in our temperature range between a free radical, R, and acetylene is addition. The model predicts the radical species that are present at the largest concentrations to be $C_2H_3Br_2$, C_2H_3, and Br. In the case of a brominated radical, the adduct would decompose rapidly by bromine atom elimination as discussed earlier. In the case of free radicals that do not contain bromine, the adduct would not decompose as easily and, if formed in sufficient concentrations, these adducts could add to the parent molecule, vinyl bromide, giving brominated radicals which would then be expected to decompose rapidly by bromine atom elimination. The addition of atomic bromine to acetylene was considered earlier. When those reactions of this nature not already present in the model were added, there was no change in the quality of fit to the experimental data at either the upper or lower end of

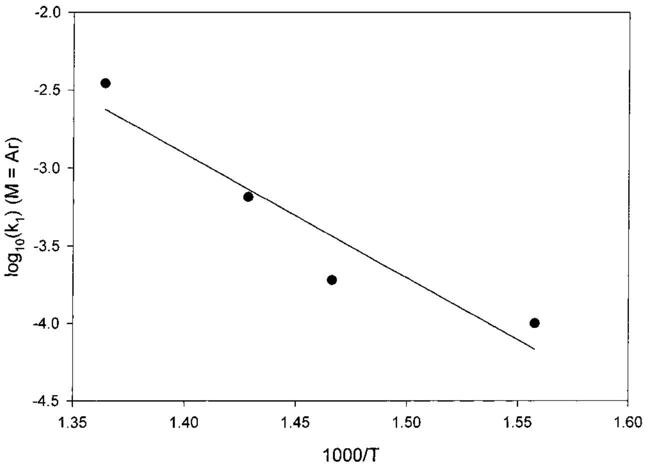

Figure 8. Temperature dependence of the rate constant for $C_2H_3Br + Ar \rightarrow C_2H_2 + HBr + Ar$.

the temperature range of the experiments at a pressure of 16 kPa. We conclude from these results that reactions of free radical intermediates with acetylene, in the concentrations produced under our reaction conditions, are already adequately represented by the model.

HBr reacts readily with small organic free radicals[15] with a typical preexponential factor of about 7×10^8 L mol^{-1} s^{-1} and an activation energy of roughly -5 kJ mol^{-1}. With these parameters, the calculated rates for reactions of organic free radicals with HBr were roughly two to 3 orders of magnitude larger than the reactions of the same free radicals with acetylene. The calculated effect of these reactions of HBr was not noticeable within the scatter in the experimental data over the full range of pressures and temperatures covered by our experiments. This, together with the good linearity of plots of product yield against reaction time, gives confidence that secondary reactions of reaction products with free radical intermediates do not have a kinetic effect on the reaction at the small extents of conversion of our experiments. This does not, however, mean that secondary reactions involving reaction products do not occur. Indeed, the analysis of reaction rates indicated that atomic bromine reacts with C_2H_2, C_2H_4, and 1,3-C_4H_6 at a substantial rate. However, because these reactions are effectively equilibrated they do not have a kinetic effect on the yields of the measured reaction products.

Figure 7(b) indicates the agreement with experiment obtained when the model was used to calculate the variation in the yields of C_2H_2, C_2H_4, and 1,3-C_4H_6 when the pressure was increased from 16 kPa to approximately 80 kPa by adding argon to a constant partial pressure of 16 kPa of vinyl bromide. Experiments of this nature were made at four temperatures between 636 and 733 K and the rate constants obtained by fitting $k_{1(b)}$ to the data are presented in Arrhenius form in Figure 8. Within the limitations imposed by the small number of temperatures examined and the limited accessible range of pressures and temperatures, the data of Figure 8 lead to a preexponential factor of approximately 2×10^8 L mol^{-1} s^{-1} and an activation energy of 150 kJ mol^{-1}. The reaction is clearly in its second-order region but the pressure range attainable in our apparatus is far too short to make a meaningful fundamental analysis of the falloff. It is interesting to note, however, that the activation energy we obtain for reaction 1(a) is close to that obtained in the toluene jet experiments in the literature[2] where the third bodies were primarily polyatomic, whereas the activation energy we obtain for reaction 1(b) where the third body is argon is in good agreement with the shock tube experiments in which the bath gas was Ar or Ne.[4,5] The decrease in both the activation energy and preexponential factor when vinyl bromide is replaced with the much less efficient collider, argon, is at least in qualitative agreement with results reported for the elimination of HBr from C_2H_5Br.[24] However, the relatively low precision in the Arrhenius parameters resulting from the very limited range of conditions examined in our experiments with argon preclude any detailed analysis of this effect.

Summary

We have developed a concise mechanism which quantitatively accounts for the production of C_2H_2, C_2H_4 and 1,3-C_4H_6 in the thermal decomposition of vinyl bromide. We have applied kinetic modeling to this mechanism to calculate Arrhenius parameters for both the molecular and the free radical decomposition channel. The results for the molecular channel are in excellent agreement with high temperature data in the literature, and we believe that the available experimental data in pure vinyl bromide are adequately represented by our Arrhenius expression at temperatures from approximately 600 K to 2000 K. The kinetic parameters for the molecular channel are different when the bath gas is argon and we have presented an analysis of the temperature dependence of the rate constants for this reaction in argon. We have also calculated Arrhenius parameters for the free radical decomposition channel and for the abstraction of hydrogen from the parent molecule by C_2H_3. We are unaware of any previous determination of the Arrhenius temperature dependence of the rate constants for these reactions. The activation energy for this reaction of C_2H_3 with C_2H_3Br is smaller than the value of 121 kJ mol^{-1} reported for abstraction of hydrogen by C_2H_5 from ethylene[18] and may indicate activation of one or more of the C−H bonds in vinyl bromide by the bromine atom. Analysis of the mechanism indicates that reactions of atomic bromine and brominated free radicals, although important, are not kinetically limiting for the measured hydrocarbon reaction products. On the other hand, it appears that reactions of the vinyl radical can provide kinetic control over specific reaction products. This observation suggests that the thermal decomposition of vinyl bromide might find some use as a source of kinetic data for reactions of the vinyl radical at temperatures from roughly 600 K to 800 K.

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