*Studies in the Pyrolysis of Organic Bromides. Part I. The Kinetics of the Decomposition of Allyl Bromide.**

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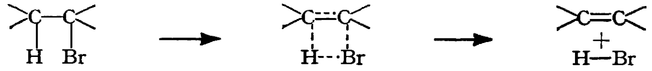
The pyrolysis of allyl bromide in the temperature range 320—380° has been shown to be a homogeneous first-order process, involving an initial rupture of the C–Br bond. The rate constants are represented by the expression $k = 2{\cdot}11 \times 10^{12}\exp(-45{,}400/\boldsymbol{R}T)$ (sec.$^{-1}$), the activation energy being in good agreement with the thermochemically determined C–Br bond dissociation energy (45·5 kcal. mole^{-1}). The overall reaction is, however, complex, and a reaction scheme has been suggested which explains the observed facts.

Introduction to a Series of Papers.

THE organic bromides, which decompose with the formation of hydrogen bromide and an olefin, form an interesting field for the study of the mechanism of gas-phase organic reactions. In all cases of saturated organic bromides examined previously, and to be described in the present series of papers, the stoicheiometry is well represented by the equation $C_nH_{2n+1}Br \longrightarrow C_nH_{2n} + HBr$, no appreciable side reaction being observed. *A priori*, two reasonable mechanisms can be envisaged. The first is a direct unimolecular splitting out of hydrogen bromide through a four-centre transition state as was indeed



discussed in connection with the pyrolysis of ethyl bromide (Vernon and Daniels, *J. Amer. Chem. Soc.*, 1933, **55**, 922; Fugassi and Daniels, *ibid.*, 1938, **60**, 771; Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 756) and of *tert.*-butyl bromide (Kistiakowsky and Stauffer,

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* A preliminary account of this work was given in *J. Chem. Phys.*, 1949, **17**, 1350.

J. Amer. Chem. Soc., 1937, **59**, 165). The second possibility is the initial breaking of a C–Br bond, previously considered by Daniels and Veltman (*loc. cit.*). These authors showed that, after the initial rupture, two courses were conceivable, the first leading to a radical non-chain mechanism; the second to a chain mechanism. The isolation and identification of examples of these processes form the subject of the present series of papers.

It may be that more than one type of mechanism is simultaneously concerned in the pyrolysis. Inhibition of radical-chain reactions has been achieved with nitric oxide (Staveley and Hinshelwood, *Nature*, 1936, **137**, 29) and with propene (Rice and Polly, *J. Chem. Phys.*, 1938, **6**, 273) through the interception of a chain-propagating radical by either of the following reaction steps :

$$\mathrm{R + NO \longrightarrow RNO}$$

$$\mathrm{R + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_2\overset{\frown}{-CH-}CH_2 + RH}$$

Thus it is to be expected that chain mechanisms involving bromine atoms would be eliminated by a reaction involving an attack on the propene molecule by a bromine atom :

$$\mathrm{Br + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_2\overset{\frown}{-CH-}CH_2 + RH}$$

Szwarc (*J. Chem. Phys.*, 1948, **16**, 128; Szwarc, Ghosh, and Sehon, *ibid.*, 1950, **18**, 1142) has developed a flow method, with toluene both as carrier gas and as chain inhibitor, for studying the rate of breaking of a C–Br bond. The reaction scheme is

$$\mathrm{R{-}Br \longrightarrow R + Br}$$

$$\mathrm{Br + C_7H_8 \longrightarrow C_7H_7 + HBr}$$

$$\mathrm{2C_7H_7 \longrightarrow C_{14}H_{14}}$$

This technique has been applied to benzyl and allyl bromides (Szwarc, Ghosh, and Sehon, *loc. cit.*) and to methyl bromide (Szwarc and Sehon, *ibid.*, 1950, **18**, 1685), but is limited to alkyl bromides without β-hydrogen atoms. The reason for this limitation will emerge later in this series. This view is supported by the work of Blades and Murphy (*J. Amer. Chem. Soc.*, 1952, **74**, 6219), who found negligible dibenzyl formation in the cases of ethyl, *n*-propyl, and *sec.*-propyl bromides. A fuller discussion of this point will be given in Part III which follows.

Although early work on the pyrolysis of bromides by Lessig (*J. Phys. Chem.*, 1932, **36**, 225), Vernon and Daniels (*loc. cit.*), and Fugassi and Daniels (*loc cit.*) was carried out in scrupulously clean reaction vessels, Daniels and Veltman (*loc. cit.*) and Kistiakowsky and Stauffer (*loc. cit.*) have shown the necessity of using vessels seasoned by contact with the reaction products in order to achieve reproducibility. All the work to be described in the present series was done in seasoned vessels. A further important factor noted by all the previous workers in this field is the marked catalytic effect of oxygen upon the pyrolysis. For this reason it is important that all traces of oxygen be removed from the reaction system.

Some possible mechanisms involving an initial splitting of a C–Br bond have been discussed by Daniels and Veltman (*loc. cit.*) in the case of ethyl bromide. The first is a non-chain radical mechanism

$$\mathrm{C_2H_5Br \xrightarrow{k_1} C_2H_5 + Br}$$

$$\mathrm{Br + C_2H_5Br \xrightarrow{k_2} C_2H_4Br + HBr}$$

$$\mathrm{C_2H_4Br + C_2H_5 \xrightarrow{k_3} C_2H_4 + C_2H_5Br}$$

For such a mechanism, the overall rate constant equals that for the initial step. Recent estimates of the bond dissociation energy of C–Br in ethyl bromide, ~67 kcal. mole^{-1}, enable this mechanism to be eliminated in view of the magnitude of the observed activation energy (53 kcal. mole^{-1}). A second mechanism involves chain propagation through the unstable bromoethyl radical: $C_2H_4Br \xrightarrow{k_3} C_2H_4 + Br$, instead of the third step in the foregoing scheme. If, for example, the chain-termination step is

$$C_2H_4Br + Br \xrightarrow{k_4} \text{end of chain}$$

the overall reaction will be of first order and the rate constant given by $k = (k_1k_2k_3/k_4)^{\frac{1}{2}}$, so that the activation energy, $E = \frac{1}{2}(E_1 + E_2 + E_3 - E_4)$ could be much less than that required to break the C–Br bond.

Evidence that chains may play a part in the pyrolysis of ethyl bromide was obtained by a study of the photolysis and pyrolysis of ethyl bromide–acetaldehyde (Roof and Daniels, *J. Amer. Chem. Soc.*, 1940, **62**, 2912; Roof, *ibid.*, 1944, **66**, 358). These reactions were studied at a temperature where ethyl bromide decomposes only slowly and acetaldehyde is quite stable. The thermal decomposition of the mixture was explained in terms of reaction chains initiated in the acetaldehyde by the radicals formed in the ethyl bromide decomposition. The photolysis could be interpreted as a photosensitisation of the ethyl bromide decomposition, which in turn started chains in the acetaldehyde.

The pyrolysis of methyl bromide has been studied by Meissner and Schumaker (*Z. physikal. Chem.*, 1940, *A*, **185**, 435). The reaction was homogeneous and resulted in the formation of carbon, hydrogen bromide, and methane, the last two substances in the approximate ratio of 2 : 1. The ratio of final to initial pressure was about 1·4. The kinetics of the reaction were complex, retardation by the products being observed. On this evidence, Whittingham (*Discuss. Faraday Soc.*, 1947, **2**, 175) advanced the following mechanism:

$$CH_3Br \longrightarrow CH_2 + HBr$$
$$CH_2 + CH_2 \longrightarrow CH_4 + C$$

The possibility of a chain mechanism cannot, however, on the evidence be ruled out.

The object of the present series of papers is to investigate the mechanism of pyrolysis of organic bromides, and in particular to isolate and study the unimolecular process. Two questions arise. (i) How do the parameters of the rate expression for unimolecular decomposition vary with alteration in structure? (ii) How does the rate of unimolecular decomposition vary in a homologous series?

EXPERIMENTAL

Apparatus and Experimental Technique.—The experiments were carried out by using a metal-bath thermostat, bismuth solder being used as the bath fluid. The bath consisted of a cylindrical metal pot of diameter 12″ and depth 12″ to which was attached a flange. To the flange was bolted a circular metal plate carrying eight wells sealed at the bottom to hold the reaction vessels. The top also supported a stirrer bearing and contained a number of holes for the introduction of a thermoregulator and of thermocouples. The outside of the pot was covered with asbestos paper and wound with resistance wire. The bath was mounted on bricks and surrounded with a cylindrical jacket, the intervening space being packed with asbestos wool. This gave about 6″ of insulating material in all directions. Temperature control was obtained to about ±025° by a combination of energy regulator and bimetallic thermoregulator. No horizontal temperature gradient could be detected in any of the wells, but there was a vertical gradient of about 0·5°. Temperatures were measured with a nichrome–eureka thermocouple, which had been calibrated by the National Physical Laboratory and was considered to be accurate within ±0·5°.

Since the reaction proceeds with an increase in pressure, it was decided to measure the rate by determining the rate of this increase. Also since hydrogen bromide is produced in the reaction, it was necessary to use an all-glass reaction vessel. Pressures were measured by means of a glass diaphragm gauge shown in Fig. 1. This is a modified form of that used by Karrer, Wulf, and Johnston (*J. Ind. Eng. Chem.*, 1922, **14**, 1015). The diaphragm *A* is made by blowing a thin bulb and then flattening the end in a flame. To the tube is sealed a frame *B* to which are attached two platinum wires *C* and *D*. The former, in the shape of a **V**, rests firmly against the diaphragm, so as to follow its movements; *D* may be adjusted through the seal *E*, so as just to make contact with C. The diaphragm is then mounted in the tube *F* and the wires sealed into the mercury cups *G*. To facilitate the sealing, the platinum wires were first welded to nickel and then to tungsten. When the pressure is the same on each side of the diaphragm the wires are adjusted so as just to make contact. A small pressure on the upper side suffices to break the contact as indicated by the inclusion of a torch bulb and battery in the external circuit. This gauge zero, the excess pressure required to break the contact, can be subtracted from all subsequent pressure readings to give the actual pressure on the lower side of the diaphragm. The diaphragm gauge was used as a null instrument, pressures being read on a mercury manometer. The accuracy was within ±0·5 mm.

The vacuum system is shown in Fig. 2. The reaction vessel *A* was cylindrical, of about 250 c.c. capacity, and to it was attached the diaphragm gauge *B*. A side-arm *C* was connected to the vessel by capillary tubing so as to minimise dead space. The side-arm and connecting tubing were wound with nichrome wire through which a current was passed to prevent condensation. The reaction system was isolated from the remainder of the apparatus by the vacuum tap *D*, lubricated with Silicone grease. A liquid-air trap *G*, which could be isolated from the rest of the system by means of taps *E* and *F*, was used for condensing out the products at the end of a run. The removable side-arm *H* facilitated their removal from the system. To the vacuum line were attached two 5-l. flasks *I* and *J*, which could be used for gas storage. One of these had a narrow tube sealed on the bottom to permit condensation of non-permanent gases. The manometer *K* and a by-pass capillary two-way tap *L*, which allowed a fine adjustment of the pressures, completed the vacuum line. The apparatus was evacuated by a two-stage rotary oil pump, the large-bore tap *M* being used for rapid pumping. As it was found that the vibration of the pump tended to make the pressure readings somewhat erratic, during a run an exhausted 5-l. flask was used as a vacuum reservoir.

FIG. 1. *The diaphragm gauge.*

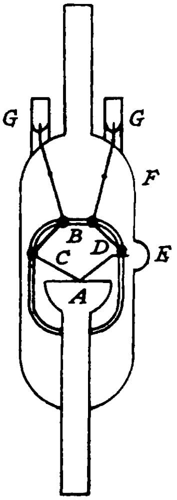
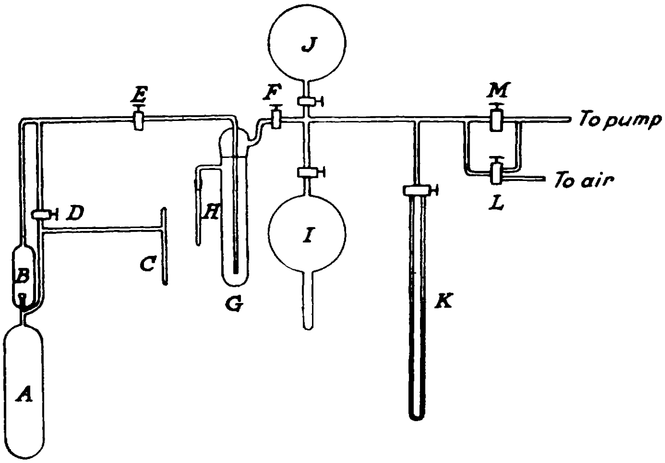


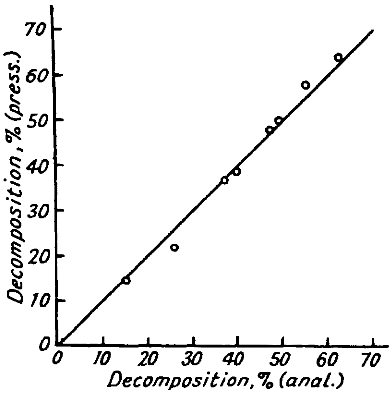
FIG. 2. *The reaction system and vacuum line.*



At the commencement of a run, a small phial filled with previously degassed allyl bromide was introduced into the side-arm *C*. This was then cooled in liquid air, and the top sealed off. The system was then evacuated to about 10^{-4} mm., and the reaction vessel isolated by closing the tap *D*. The gauge zero was then determined. By heating *C*, the allyl bromide was rapidly distilled into the reaction vessel, and the pressure measured as a function of time. At the end of a run the system was carefully exhausted, trap *G* surrounded with liquid air, and the tap *F* closed. Opening *C* caused the products to distil into *G*. Tap *E* was then closed and the products were distilled into *H*, from which they could be removed. Between runs the vacuum system was thoroughly exhausted. In order to ascertain whether the sealing-off technique affected the reaction an alternative method of introducing the allyl bromide was tried. It consisted of instantaneously connecting a hot reservoir containing allyl bromide vapour to the reaction system. By varying the temperature of the reservoir different pressures of allyl bromide could be introduced. There was no detectable difference between the runs initiated in this way and those carried out in the manner described previously.

In the case of runs in the presence of added gases, the technique was slightly different. With the permanent gases, the allyl bromide was introduced in the normal manner, the apparatus exhausted, and the gauge zero measured. The gas was then admitted to the system from the reservoir, and excess removed by pumping. The pressure could then be read on the manometer, or in the case of low pressure on a McLeod gauge. Tap *D* was then closed, and the reaction started. In the case of propene, indentations were made in the side-arm *C* about ½″ from the bottom. After the apparatus was exhausted, propene was admitted, tap *D* shut, and the propene in the reaction vessel condensed out with liquid air. The propene remaining in the vacuum system was then taken back to the reservoir. The gauge zero was then determined, and the propene distilled into the reaction vessel from *C*. The propene pressure was then measured. The propene was then condensed out again in *C*, collecting in the bottom, and the top of *C* blown off. The phial of allyl bromide was then introduced, the side-arm sealed off, and the apparatus exhausted. The run was then started in the normal fashion. The indentations in the side-arm *C* prevented the relatively "hot" phial of allyl bromide from coming in contact with the condensed propene. An alternative technique was to introduce the allyl bromide in the usual manner into *C*, cool it with liquid air, and exhaust the vessel. The liquid air was then replaced by carbon dioxide–ether and finally a freezing mixture. Propene was then admitted to the system, and the pressure measured. The run could then be commenced as usual. In the case of bromine, the former procedure was followed.

FIG. 3. *The percentage decomposition as determined from pressure measurements plotted against that determined by analysis of the hydrogen bromide produced.*



As a check on the rate constants obtained from the pressure–time curves, an alternative procedure involving the determination of the hydrogen bromide evolved from a given weight of allyl bromide was employed. A reaction vessel fitted with a side-arm was joined to the vacuum line. Into the side-arm was placed a phial containing a weighed amount of allyl bromide. This was then distilled into the reaction vessel, outgassed by successive evaporation and freezing, and the reaction vessel sealed off. Six vessels were introduced into the thermostat, which had had its temperature raised by about 2° to allow for the cooling effect of the vessels, and were then removed after given intervals of time, their tips were broken under standard alkali, and the hydrogen bromide was estimated.

The allyl bromide used in these experiments was obtained by drying a commercial sample (over P_2O_5) and fractionally distilling it through a 3′ column packed with glass helices. A distillate of constant b. p. and refractive index was collected, *viz.*, b. p. 69·8°/760 mm., n_D^{20} 1·4692. The most recent literature values are b. p. 69·9°/760 mm., n_D^{20} 1·4693 (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468).

The Nature and Order of the Reaction.—From a study of the pressure–time curves, it was found that the ratio of the final to initial pressure approached 1·5, an observation best explained on the basis of an overall reaction of the type $C_3H_5Br \longrightarrow \frac{1}{2}(C_6H_8) + HBr$. If $(p_0 - p)$ is the pressure of allyl bromide at time *t*, the pressures of C_6H_8 and HBr are respectively $\frac{1}{2}p$ and p. If the total pressure at time *t* is *P*, then

$$P = p_0 - p + \tfrac{1}{2}p + p = p_0 + \tfrac{1}{2}p.$$

The percentage decomposed (*D*) is thus given by $D = 100p/p_0 = 200(P - p_0)/p_0$. Again, the percentage undecomposed may be calculated from the hydrogen bromide produced. In Fig. 3 the percentage decomposed, calculated from the mean of about six pressure runs, is plotted against the percentage decomposed as determined by the analytical experiments. The points all lie close to the straight line of unit slope, passing through the origin, thus justifying the use of pressure–time curves in determining the rate of decomposition.

The order of the reaction was established by plotting the logarithm of the percentage undecomposed against time. For both the pressure and the analytical experiments, good straight lines were obtained up to about 60% decomposition. Further, as is shown in the following Table, the rate constants obtained by the two methods are in essential agreement.

Temp.	10^5k_1 (sec.$^{-1}$) (pressure)	10^5k_1 (sec.$^{-1}$) (analytical)
320°	3·89	3·96
340	13·7	14·0

Each entry in the table is the mean of five runs. The reaction is thus of the first order.

The homogeneity of the reaction was established by packing reaction vessels with glass tubing so as to give surface-volume ratios of approximately 1, 2, and 3. By plotting the velocity constants as a function of *S*/*V*, and extrapolating to *S*/*V* = 0, the homogeneity of the reaction could be estimated. The results are shown below, the runs being done at 320°:

FIG. 4. *The percentage decomposition at four temperatures as a function of time.* I, 380°; II, 360°; III, 340°; IV, 320°.

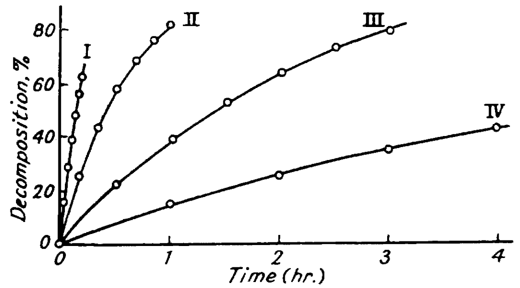
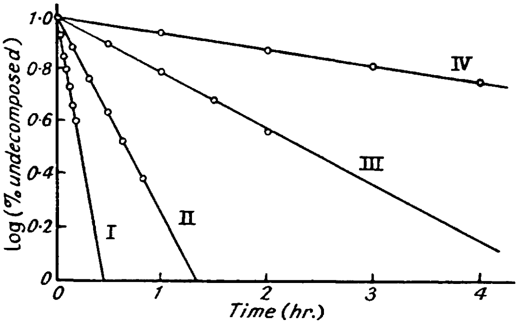


FIG. 5. *The logarithm of the percentage decomposition at four temperatures as a function of time.* Temperatures as for Fig. 4.



	p_0 = 210 mm.				p_0 = 470 mm.			
S/*V* (cm.$^{-1}$)	0	1·2	2·1	3·0	0	1·2	2·1	3·0
10^5k_1 (sec.$^{-1}$)	(3·10)	3·26	3·44	3·79	(3·82)	3·86	3·92	4·06

As the surface-volume ratio of the reaction vessel used for the pressure runs was ~1 cm.$^{-1}$, it can be estimated that the reaction is about 95% homogeneous at 200 mm. and 99% homogeneous at 500 mm. During the reaction, a carbonaceous deposit developed on the walls of the vessel. As the pressure runs were done in seasoned vessels, it was of interest to see if the constants determined for cleaned and for seasoned vessels differed: the respective values of k_1 were $3{\cdot}89 \times 10^{-5}$ and $3{\cdot}86 \times 10^{-5}$ sec.$^{-1}$, so the wall coating has no appreciable effect on the rate. It may thus be concluded that the reaction is predominantly homogeneous.

To test the completeness of the reaction, with respect to elimination of hydrogen bromide, sealed tubes (P_0 ~900 mm.) were left in the thermostat for 60 hr. at 320°. The mean decomposition was 85%.

Attempts to isolate the C_6H_8 hydrocarbon at the end of a run were not successful. As the kinetic apparatus was only capable of handling small quantities of allyl bromide, product runs were done in a 5-l. reaction vessel. The liquid reaction products were condensed out after a run and fractionated through a small column. Evidence was obtained for the presence of three substances in small quantities. The first fraction had b. p. 58—59°, n_D^{20} 1·4402 (Found: C, 30·7; H, 4·6; Br, 65·0%), and can reasonably be regarded as a mixture of 1-bromopropene (b. p. 60°; n_D^{20} 1·4554. Calc.: C, 29·8; H, 4·1; Br, 66·1%) and *iso*propyl bromide (b. p. 59·4°; n_D^{20} 1·4228. Calc.: C, 29·3; H, 5·7; Br, 65·0%). The last fraction, which boiled at about 80°, had n_D^{25} 1·4908 (Found: C, 84·9; H, 7·7; Br, 7·5%). Thus complete separation from bromo-compounds was not attained. However, a measurement of the absorption spectrum showed that the fraction was largely benzene.*

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* The author is indebted to Dr. E. M. F. Roe and Dr. R. N. Beale, of the Royal Cancer Hospital, for this measurement.

Results.—The results of the pressure experiments are shown in the following Table. The initial pressures were obtained by extrapolation to zero time, and the velocity constants obtained from the slope of the log (% undecomposed)–time curves. The mean percentage decomposition–time curves are shown in Fig. 4, and the logarithmic plots in Fig. 5. The data shown

$T =$ 320°		340°		360°		380°	
p_0 (mm.)	10^5k (sec.$^{-1}$)	p_0 (mm.)	10^5k (sec.$^{-1}$)	p_0 (mm.)	10^5k (sec.$^{-1}$)	p_0 (mm.)	10^5k (sec.$^{-1}$)
460	4·03	670	13·5	510	47·7	490	136
430	3·97	474	13·8	494	45·8	400	132
398	3·87	420	13·8	445	45·3	400	130
367	3·88	410	13·9	432	46·0	362	132
344	3·95	331	13·7	338	46·5		
				312	47·5		

above were fitted to the Arrhenius equation $k = 2{\cdot}11 \times 10^{12} \exp(-45{,}400/\boldsymbol{R}T)$ (sec.$^{-1}$), the Arrhenius plot being shown in Fig. 6.

A number of experiments were done at pressures below 300 mm., in order to investigate the effect of pressure on the velocity constant. As the velocity constant at low pressures depends rather critically upon the extrapolated initial pressure, the accuracy of these results does not warrant an exhaustive analysis of them, so it suffices to say that a fall in velocity constant is observed for pressures <300 mm.

FIG. 6. *The Arrhenius plot.*

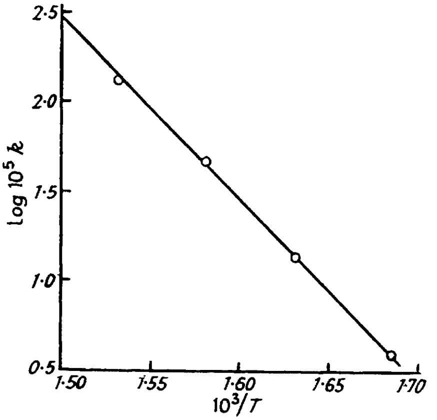
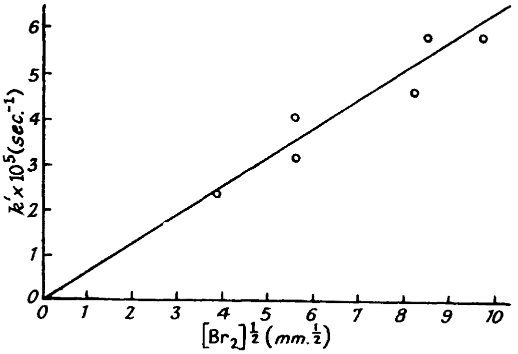


FIG. 7. *The initial rate of decomposition as a function of the square root of the bromine pressure.*



As oxygen has been reported to have marked effects upon the pyrolysis of ethyl and the propyl bromides, runs were carried out at 320° with oxygen pressures of 0·9 and 10 mm. The initial allyl bromide pressures were 294 and 378 mm., respectively, and so the velocity constants in the absence of oxygen would be $3{\cdot}79 \times 10^{-5}$ and $3{\cdot}94 \times 10^{-5}$ sec.$^{-1}$, respectively. The observed velocity constants were $3{\cdot}75 \times 10^{-5}$ and $3{\cdot}99 \times 10^{-5}$ sec.$^{-1}$, indicating that oxygen at small partial pressures has no effect on the reaction.

The fall in rate constant as the initial pressure of bromide decreases has already been referred to. It was originally interpreted as the fall in rate constant predicted by Lindemann's theory. The effect of added nitrogen and hydrogen upon the rate constant was thus investigated, and it appeared that, whereas nitrogen has no effect upon the rate, hydrogen is capable of restoring the low-pressure rate to its limiting value. It should be emphasized that in view of the chemical complexity of the overall reaction, to be discussed in the next section, it is now considered unlikely that the fall in the rate constant and its restoration by hydrogen can be interpreted in terms of a Lindemann mechanism.

The effect of bromine on the rate of decomposition was investigated. An increase in the rate was observed, but because of the possibility of altered stoicheiometry of the reaction only the initial fractional rate of pressure increase was derived from the results. This quantity $(1/P_0)(\mathrm{d}P/\mathrm{d}t)_0 = k'$ is shown as a function of the square root of the bromine pressure in Fig. 7. It is seen that a linear relation exists. The bromine was observed to disappear from the reaction system fairly rapidly, and for this reason the initial rates were employed.

The reaction was studied in the presence of varying amounts of propene,* the results being shown in the following Table, where p_i is the partial pressure of propene. It is seen that the

$T = 380°$

p_i (mm.)	0	43	124	129	0	82	177
p_0 (mm.)	400	410	385	390	306	303	275
10^5k (sec.$^{-1}$)	132	127	127	132	115	116	124

rate is independent of the propene pressure. This observation rules out the possibility of long bromine atom chains being concerned in the decomposition.

DISCUSSION OF RESULTS

It has been shown that the gas-phase pyrolysis of allyl bromide in the temperature range 320—380° is a homogeneous, first-order process. In calculating the rate constants from the pressure–time curves, the equation $C_3H_5Br \longrightarrow \frac{1}{2}(C_6H_8) + HBr$ was employed. This was consistent with the observed pressure change, and the percentage decomposition calculated on this basis agreed with that derived from direct titration of the hydrogen bromide produced. The products observed were hydrogen bromide, benzene, and a carbonaceous coating. A product which would not have been detected by the technique used in the present investigation was propene. This has been observed by Szwarc, Ghosh, and Sehon (*loc. cit.*) to the extent of 20—30% of the hydrogen bromide produced. This last observation, together with the complete absence of any of the polymers of allene, would rule out the process $C_3H_5Br \longrightarrow C_3H_4 + HBr$, $2C_3H_4 \longrightarrow C_6H_8$, involving a direct elimination of hydrogen bromide. The probable initial step is thus $C_3H_5Br \longrightarrow C_3H_5 + Br$, an assumption consistent with the observed C–Br dissociation energy (Gellner and Skinner, *J.*, 1949, 1145), *viz.*, 45·5 kcal. mole^{-1}. The value observed by Szwarc *et al.* (*loc. cit.*) by the toluene-carrier technique is 47·5 kcal. mole^{-1}. To account for the propene, and also the carbonaceous deposit, a heterogeneous reaction of allyl radicals may be postulated: $C_3H_5 + C_3H_5 \longrightarrow C_3H_6 + \frac{1}{x}(C_{3x}H_{4x})$. The allyl radicals are considered to be sufficiently long-lived to reach the walls of the reaction vessel. Benzene can arise from the interaction of two bromoallyl radicals formed by attack of bromine on allyl bromide: $Br + C_3H_5Br \longrightarrow HBr + C_3H_4Br$; $C_3H_4Br + C_3H_4Br \longrightarrow C_6H_6 + 2HBr$. This reaction may or may not occur homogeneously. The overall mechanism may then be represented by

$$\begin{aligned} C_3H_5Br &\longrightarrow C_3H_5 + Br \\ Br + C_3H_5Br &\longrightarrow C_3H_4Br + HBr \\ C_3H_5 &\longrightarrow \tfrac{1}{2}C_3H_6 + \frac{1}{2x}(C_{3x}H_{4x}) \quad \text{(surface)} \\ C_3H_4Br &\longrightarrow \tfrac{1}{2}C_6H_6 + HBr \end{aligned}$$

and the overall reaction by

$$C_3H_5Br \longrightarrow HBr + \tfrac{1}{4}C_3H_6 + \tfrac{1}{4}C_6H_6 + \frac{1}{4x}(C_{3x}H_{4x})$$

It remains to account for the 1-bromopropene and the *iso*propyl bromide found in the products. These may be regarded as the result of side reactions. The former could arise from

$$C_3H_5Br + CHBr\overset{\frown}{—CH—}CH_2 \longrightarrow CHBr{:}CH{\cdot}CH_3 + C_3H_4Br$$

and, being a substituted vinyl bromide, would be expected to be stable in the temperature range considered. The *iso*propyl bromide, on the other hand, would result from a normal addition of hydrogen bromide to propene.

The decrease in rate constant with decreasing initial pressure of allyl bromide, and the restitution of the rate with hydrogen, might be taken as indicative of the decrease in rate constant with decreasing pressure predicted by Lindemann's theory of unimolecular reactions. However, recent calculations by Slater (*Phil. Trans.*, 1953, **246**, 57) suggest

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* The author is indebted to Imperial Chemical Industries Limited, Billingham Division, for a gift of propene.

that the observed pressure range is far too high to account for the falling off in this manner. As a more probable alternative it is suggested that, as the pressure falls, one of the steps subsequent to the initial breaking of the C–Br bond may become slow. The effect of hydrogen could then be explained by its chemical intervention.

Additional confirmation of the non-chain character of the reaction comes from the observed lack of inhibition of the reaction by propene. Again, this reaction is unique in comparison with other bromides studied, in that oxygen has no effect upon the rate. This would suggest the impossibility of initiating chains in allyl bromide, and can be interpreted in terms of the stability of the bromoallyl radical with respect to a splitting off of a bromine atom:

$$\mathrm{CH_2\overset{\curvearrowright}{-CH-}CHBr} \longrightarrow \mathrm{CH_2{\cdot}CH{\cdot}CH + Br}$$

Confirmation of the presence of bromine atoms in decomposing allyl bromide comes from an unpublished observation by P. J. Thomas that the presence of decomposing allyl bromide accelerates the decomposition of certain other organic bromides. It may reasonably be concluded that allyl bromide decomposes by a bromine atom non-chain mechanism.

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