Studies in the Pyrolysis of Organic Bromides. Part II. The Pyrolysis of* n*-Propyl Bromide.*†

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n-Propyl bromide decomposes into propene and hydrogen bromide in the temperature range 300—380°, according to a rate equation of order 1·5. The rate constants were expressible as

$$k_{1\cdot5} = 7{\cdot}24 \times 10^{10} \exp(-33{,}800/\boldsymbol{R}T) \ (\text{mole}^{-\frac{1}{2}}\ \text{c.c.}^{\frac{1}{2}}\ \text{sec.}^{-1})$$

A great increase in the surface : volume ratio had only a relatively small effect upon the rate. Propene, on the other hand, strongly inhibited the reaction. It is concluded that the reaction is homogeneous and that the mechanism is of a chain type, the initiating step being the breaking of a carbon–bromine bond.

THE first work reported on the pyrolysis of the propyl bromides was by Aronstein (*Rec. Trav. chim.*, 1882, **1**, 134), who showed that both *n*- and *iso*-propyl bromide decompose at high temperatures to yield propene and hydrogen bromide. Nef (*Annalen*, 1901, **318**, 14) showed that when *n*-propyl bromide was passed through a pumice-filled tube at 500°, practically the calculated yield of propene was produced. Lessig (*J. Phys. Chem.*, 1932, **36**, 2325) verified that the reaction in the case of the propyl bromides was $C_3H_7Br \rightarrow C_3H_6 + HBr$, the propene being identified both by absorption in bromine water and by combustion. First-order rate coefficients calculated from the rate of pressure increase in clean vessels on the basis of the above reaction were found to increase markedly with increasing initial pressure. The reaction was shown to be homogeneous, and oxygen had a strongly catalytic effect. No activation energy was reported. However, on the basis of some unpublished results, Daniels and Veltman (*J. Chem. Phys.*, 1939, **7**, 756) quote an activation energy of 36 kcal.

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* Part I, preceding paper.

† A preliminary account of this work was given in *J. Chem. Phys.*, 1950, **18**, 158.

EXPERIMENTAL METHODS AND RESULTS

A commercial sample of *n*-propyl bromide was distilled through a 1-m. column packed with glass helices. The middle fractions, of constant b. p. and refractive index, were collected. The sample used for the kinetic study had b. p. 71·15° (71·00°), n_D^{25} 1·4318 (1·4318), d_4^{25} 1·3431 (1·3431), the values in parentheses being due to Timmermans ("Physical Constants of Pure Organic Compounds," Elsevier, Netherlands, 1950).

For the inhibition experiments, propene was prepared by dehydration of *iso*propyl alcohol with phosphoric oxide; it was purified by several trap-to-trap distillations through a tube containing phosphoric oxide supported on granular calcium chloride. Finally, the propene was distilled into a glass storage reservoir and thoroughly out-gassed.

The apparatus and the technique used were essentially as described in Part I, except that an aluminium block thermostat was used in place of the metal bath. Temperature control to ±0·25° was obtained, the temperatures being measured with a calibrated nichrome–eureka thermocouple.

In order to verify the stoicheiometry of the reaction, analytical runs were carried out in sealed tubes, the hydrogen bromide being determined by titration, and the propene by an estimation of the residual volume of undissolved gas. A plot of the moles of hydrogen bromide against moles of propene produced is shown in Fig. 1, the results being obtained at two different initial pressures, ~250 and ~600 mm. In view of the inaccuracy inherent in the method of estimating the propene, the agreement is quite good.

FIG. 1.

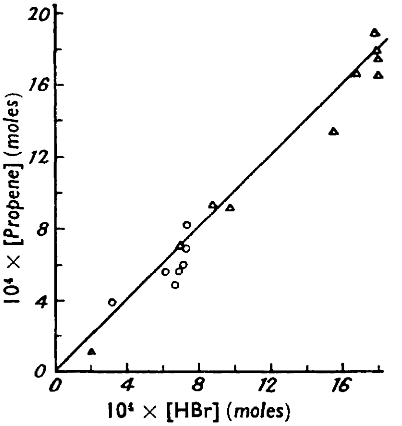

FIG. 2.

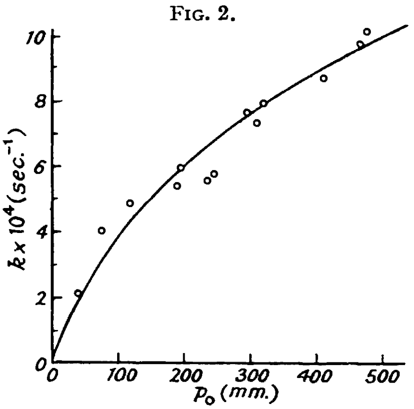

FIG. 1. *The equivalence of propene and hydrogen bromide produced in the pyrolysis of* n-*propyl bromide.*

Δ, Mean initial pressure 609 mm.; ○, mean initial pressure 256 mm. The straight line is of unit slope.

FIG. 2. *First-order rate coefficients as a function of initial pressure.*

The completeness of the reaction was tested by taking infinity measurements both of the hydrogen bromide produced and of the total pressure. Thus after *ca.* 24 hr., the mean extents of decomposition were 81·9% starting from an initial pressure of 600 mm., and 91·0% starting from 250 mm. The percentage decompositions derived from pressure measurements are shown in Table 1. The results show conclusively that an equilibrium exists, since the higher the initial pressure at any given temperature, the lower the percentage decomposition. The quantitative nature of the results is however doubtful, inasmuch as the equilibrium is not a simple one, the C_3H_7Br being either *n*- or *iso*-propyl bromide. Again, in the pressure runs, dead-space errors play some part and so the percentage decompositions recorded are lower limits. Qualitatively,

TABLE 1.

p_0 (mm.)	373	282	193	114	333	161	37·4
T	300°	300°	340°	340°	360°	360°	360°
p_∞/p_0	1·73	1·76	1·85	1·89	1·78	1·82	1·87
Decompn., %	73	76	85	89	78	82	87

at least, the observations are in favour of the equilibrium $C_3H_7Br \rightleftharpoons C_3H_6 + HBr$, and since only the early stages of the reaction have been used in calculating the kinetic constants, the complex nature of the reverse reaction may be neglected.

It has been mentioned that Lessig found the first-order constants for the pyrolysis of *n*-propyl bromide to be markedly dependent on pressure; this could be a normal Lindemann decrease in a unimolecular mechanism, or could be due to the reaction's being of a higher order. In order to settle this matter, the pressure variation of the rate was measured at 360° over a range 40—500 mm. The first-order rate constant as a function of pressure is shown in Fig. 2. It will be seen that there is no tendency to approach a limiting value as the initial pressure is increased, as would be expected for a Lindemann decrease. The results thus suggested a reaction of a higher order, and so the first-order constants were plotted against the square root of the initial pressure. A good straight line, passing through the origin, shown in Fig. 3, resulted. This was suggestive of the reaction's being of order 1·5 and so rate constants of this order were calculated which, while showing a scatter about the mean value, showed no significant trend with initial pressure. Their behaviour is to be compared with that of the first-order coefficients, which varied from $2\cdot13 \times 10^{-4}$ sec.$^{-1}$ to $10\cdot2 \times 10^{-4}$ sec.$^{-1}$ in the pressure range 40—500 mm. Similar independence of initial pressure of the constants of order 1·5 was observed at other temperatures, so it was concluded that the reaction was of this order.

FIG. 3.

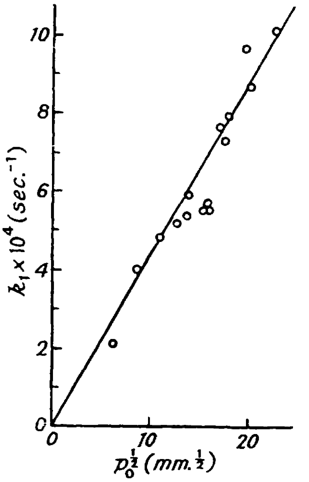

FIG. 4.

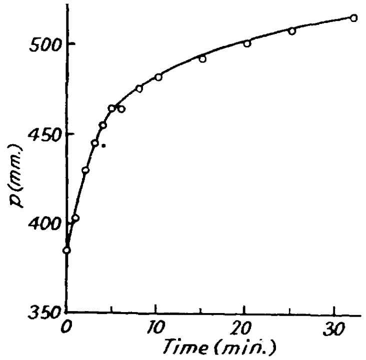

FIG. 3. *The relation between the first-order rate coefficients and the square root of the initial pressure*

FIG. 4. *The effect of oxygen on the pressure–time curve.*

Further to verify this, two analytical experiments using the sealed-tube technique, were done at 320°, each involving about a dozen analytical determinations of hydrogen bromide. The percentage decomposition as measured by the hydrogen bromide produced and interpolated from a smooth curve is shown in Table 2. These results lead to values of $k_{1\cdot5}$ of $31\cdot6 \times 10^{-3}$ and $28\cdot6 \times 10^{-3}$ mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-1}$, respectively, in fair agreement with the mean value obtained from pressure measurements, namely, $32\cdot7 \times 10^{-3}$ mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-1}$. The first-order coefficients in the two cases are respectively $2\cdot26 \times 10^{-4}$ and $1\cdot34 \times 10^{-4}$ sec.$^{-1}$.

TABLE 2.

Time (min.)	0	12	24	36	48	60
		$p_0 \sim 610$ mm.				
Decompn., %	0	16·8	30·0	38·2	45·5	51·7
		$p_0 \sim 260$ mm.				
Decompn., %	0	7·8	16·1	24·2	31·5	37·2

The pressure measurements were done in well-seasoned vessels. As seasoning by the products of reaction is rather slow, it was decided to use the observation (Part I, *loc. cit.*) that pyrolysis of allyl bromide produced a heavy carbonaceous coating on the walls of the vessel, so seasoning of the reaction vessel was effected by this means. Rate measurements on the pyrolysis of *n*-propyl bromide done in vessels thus seasoned were reproducible and consistent. In order to check the homogeneity of the reaction, a number of runs were done in a vessel whose surface : volume ratio had been increased by a factor of 17 over that of the unpacked vessel. The rate constants obtained at two temperatures are shown in Table 3, where the values for the unpacked vessel are also shown. In view of the very large increase in surface : volume ratio, the observed change in rate is very small.

TABLE 3.

Temp.	$10^3k_{1\cdot5}$ (packed)	$10^3k_{1\cdot5}$ (unpacked)	Temp.	$10^3k_{1\cdot5}$ (packed)	$10^3k_{1\cdot5}$ (unpacked)
320°	22·0	32·7	360°	166	144

Lessig (*loc. cit.*) had already commented upon the catalytic effect of oxygen on the decomposition of *n*-propyl bromide. Although the interpretation of the rôle played by oxygen in the pyrolysis of alkyl bromides is difficult, it was deemed necessary to show that, under the experimental conditions used in the present work, its effects were negligible. To this end, a number of runs were done in the presence of varying small pressures of oxygen (2—0·02 mm.). A characteristic pressure–time curve is shown in Fig. 4. An interesting feature of the curves is the abrupt change in slope, suggesting that the oxygen was used up after a certain time. This was borne out by the fact that the greater the pressure of oxygen, the greater the percentage decomposition of the bromide before the discontinuity in the slope occurs. It was also shown that when the oxygen pressure was ~0·02 mm. the effect had become very small, and so it is safe to regard the oxygen effect as being absent in the normal runs, as the vessel was always evacuated to less than 0·001 mm.

FIG. 5.

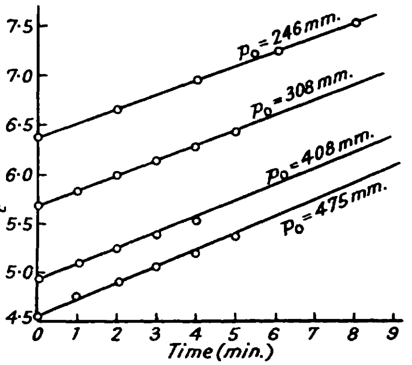

FIG. 6.

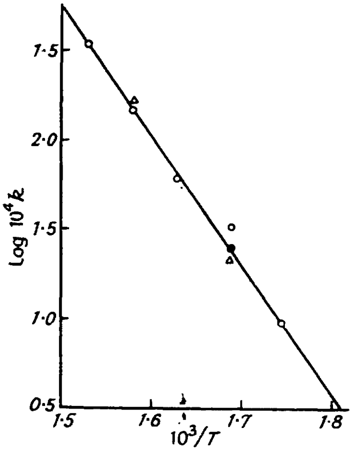

FIG. 5. *The* 1·5-*order plots at* 360°.

FIG. 6. *The Arrhenius plot.* ○, Vessel unpacked, seasoned. △, Vessel packed, seasoned. ●, Vessel unpacked, unseasoned.

TABLE 4.

Temp.	300°	320°	340°	360°	380°
No. of runs	6	8	10	15	5
$10^3k_{1\cdot5}$ (mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-1}$)	9·54	32·7	61·4	147	346

The results of the pressure investigations at different temperatures are shown in Table 4. In Fig. 5 are shown some of the 1·5-order plots (reciprocal square root of bromide pressure at time *t*, against time). The results were fitted to the Arrhenius equation $k_{1\cdot5} = 7\cdot24 \times 10^{10} \exp(-33{,}800/\boldsymbol{R}T)$ mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-1}$, the resulting plot being shown in Fig. 6.

In view of the order of the reaction, which strongly suggests a chain mechanism, the inhibiting power of propene was investigated. Because of the large partial pressures of propene required to produce maximum inhibition, it was not found possible accurately to ascertain the order of the reaction under these conditions,* so, to show the effect of increasing partial pressure

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* Dr. P. J. Thomas has since shown the maximally inhibited rate to be that of a first-order reaction. Further evidence indicates that it is indeed the unimolecular splitting out of hydrogen bromide.

of propene, the values of $k_{1\cdot5}$ at 360° are plotted against the partial pressure of propene in Fig. 7. Points are shown for both packed and unpacked vessels, and the approach of the rate to a limiting value is clearly illustrated. It is noteworthy that the ratio of final to initial pressure became greatly reduced, a fact which bears out the view expressed earlier of an equilibrium between propyl bromide and its decomposition products.

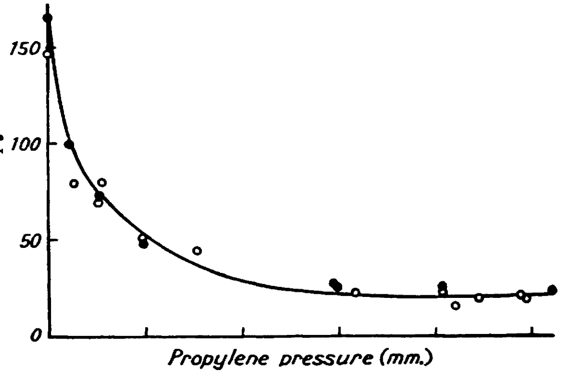

FIG. 7. 1·5-*Order rate coefficients in the presence of added propylene, showing the approach to a limiting value as the propylene pressure is increased.*

○, Unpacked vessel;
●, packed vessel.

DISCUSSION

The observed kinetic order of the decomposition of *n*-propyl bromide together with the marked inhibitory effect of propene are conclusive evidence of the existence of a chain mechanism. This conclusion is strengthened by the presence of relatively short and quite irreproducible induction periods in some of the runs. The relatively small effect on the rates of decomposition of a very large increase in the surface : volume ratio means that the reaction either is essentially homogeneous or is a heterogeneous process in which the chains are both initiated and terminated at a surface. But it is difficult to visualise such a process leading to the observed 1·5-order kinetics. The most probable explanation of the results is a homogeneous chain mechanism.

In considering the various chain mechanisms possible for *n*-propyl bromide, the obvious chain-initiation and chain-propagating steps are

$$CH_3\cdot CH_2\cdot CH_2Br \xrightarrow{k_1} CH_3\cdot CH_2\cdot CH_2 + Br$$

$$Br + CH_3\cdot CH_2\cdot CH_2Br \xrightarrow{k_2} CH_3\cdot CH\cdot CH_2Br + HBr$$

$$CH_3\cdot CH\cdot CH_2Br \xrightarrow{k_3} CH_3\cdot CH{:}CH_2 + Br$$

The fate of the *n*-propyl radical is of little importance in view of the great length of the chains (see p. 978). If, on the one hand, the *n*-propyl radicals decompose on reaching the walls of the reaction vessel, the products of this reaction would be below the limits of observation. If, on the other hand, they entered into the hydrogen-abstraction reaction

$$CH_3\cdot CH_2\cdot CH_2 + CH_3\cdot CH_2\cdot CH_2Br \longrightarrow CH_3\cdot CH_2\cdot CH_3 + CH_3\cdot CH\cdot CH_2Br$$

the effect would be to introduce a factor of 2 into the overall rate expression. Once again, the propane produced would be below the limit of observation. Conceivable chain-ending steps are

$$Br + Br + X \xrightarrow{k_6} Br_2 + X$$

$$Br + CH_3\cdot CH\cdot CH_2Br \xrightarrow{k_7} \text{end of chain}$$

Application of the usual stationary-state approximation shows that reaction (7) would lead to first-order kinetics and so may be excluded. To the same approximation, if it is assumed that X may be either C_3H_7Br or C_3H_6, then (4) leads to the observed 1·5 order with respect to *n*-propyl bromide at a given initial pressure, but the initial fractional rate is found to be independent of *n*-propyl bromide pressure, so this scheme can also be rejected.

A possible interpretation of the kinetics lies in a further analysis of the attack of a bromine atom on a *n*-propyl bromide molecule (P. J. Thomas, Thesis, University of London, 1953). If the attack is at a β-hydrogen atom, then the resultant radical may undergo dissociation as shown in (3). However, if the attack is at the α- or γ-position the radical may be assumed to be stable as regards C–Br bond breaking. It is, however, possible for such a " stopping " (S) radical to react with a *n*-propyl bromide molecule to produce a " propagating " (P) radical

$$\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2Br + C_3H_7Br \xrightarrow{k_4} CH_3{\cdot}CH{\cdot}CH_2Br + C_3H_7Br} \quad . \quad . \quad . \quad . \quad (6)$$

If it is now assumed that the P radicals are short lived, then the chain-ending step may be written as the recombination of a bromine atom and an S radical :

$$\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2Br + Br \xrightarrow{k_5} end\ of\ chain} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By using the conventional stationary-state assumption, the overall rate may be written as

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{C_3H_7Br}] = \left\{\frac{k_1k_2k_4}{k_5}\left(\frac{k_2}{k_2'}\right)\right\}^{\frac{1}{2}}[\mathrm{C_3H_7Br}]^{\frac{3}{2}}$$

where k_2 and k_2' refer to the rate constants for the production of P and S radicals by the attack of a bromine atom on a *n*-propyl bromide molecule. No precise values are available for the activation energies of the individual reactions, so it is difficult to estimate the overall activation energy. It is, however, obvious that it would be much less than the C–Br bond dissociation energy. Further experiments are being carried out by Dr. P. J. Thomas in order more firmly to establish the mechanism.

The inhibition produced by added propene may be explained by assuming (8) to be in

$$\mathrm{Br + CH_3{\cdot}CH{:}CH_2 \longrightarrow HBr + CH_2{-}\overset{\frown}{H}{-}CH_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

competition with (2) and (2′). At maximal inhibition, the chain component of the reaction would be reduced to

$$\mathrm{C_3H_7Br \longrightarrow C_3H_7 + Br}$$
$$\mathrm{Br + C_3H_6 \longrightarrow C_3H_5 + HBr}$$

which would be unobservable in the temperature range concerned, in view of the magnitude of the C–Br bond dissociation energy. This view has been confirmed by the independent studies of the maximally inhibited reaction by Thomas using *cyclo*hexene (to be published later in this series) in a static system, and by Blades and Murphy using a toluene carrier-gas technique (*J. Amer. Chem. Soc.*, 1952, **74**, 6219).

An estimate may be made of the chain length in the decomposition by using a value of the C–Br bond dissociation energy, suggested by Linnett *et al.* (*Proc. Roy. Soc.*, 1952, **216**, *A*, 361) of 67·9 kcal. Assuming a value of 10^{13} for the pre-exponential factor in the Arrhenius equation, we have $k_1 = 10^{13} \exp(-67{,}900/\boldsymbol{R}T)$. The chain length γ is thus

$$\gamma = 7{\cdot}24 \times 10^{-3}c^{\frac{1}{2}} \exp(+34{,}100/\boldsymbol{R}T)$$

where c is the concentration in mole c.c.$^{-1}$. This gives at 600° K and 300 mm. initial pressure, a chain length of the order of 10^7.

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