Studies in the Pyrolysis of Organic Bromides. Part III. The Pyrolysis of* iso*Propyl Bromide.*†

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The decomposition of *iso*propyl bromide in the gas phase has been shown to be a homogeneous, first-order reaction in the temperature range 310—350°. Propene and hydrogen bromide were the only products observed, and the first-order constants decreased during the reaction owing to an equilibrium between the products and the undecomposed bromide. Propene had no effect on the rate, the variation of which with temperature was represented by

$$k = 4{\cdot}17 \times 10^{13} \exp(-47{,}800/\mathbf{R}T)(\text{sec.}^{-1})$$

The results are consistent with a unimolecular elimination of hydrogen bromide. The rate constants maintained their normal values down to 25 mm. initial pressure of the bromide.

EARLY qualitative studies (for references see Part II) showed that the propyl bromides decomposed at high temperatures into propene and hydrogen bromide. The first attempt to study the kinetics of the pyrolysis of *iso*propyl bromide was made by Lessig (*J. Phys. Chem.*, 1932, **36**, 2335). The reaction was carried out in scrupulously cleaned vessels, but the results were not very satisfactory owing to a lack of reproducibility. It was concluded that the reaction was of the first order, although the rate coefficients showed a marked dependence upon the initial pressure of *iso*propyl bromide. Thus at 346·5°, the first-order rate coefficients were in the range 2—6 × 10^{-3} sec.$^{-1}$. It was also observed that the ratio of the final to the initial pressure was less than 2, as demanded by the equation $C_3H_7Br \longrightarrow C_3H_6 + HBr$.

EXPERIMENTAL

A commercial sample of *iso*propyl bromide was twice distilled through a 1-m. column packed with glass helices. It then had b. p. 59·32°/760 mm. (59·32°), n_D^{15} 1·4285 (1·42847), the values in parentheses being those of Timmermans and Martin (*J. Chim. phys.*, 1929, **25**, 423). During the work comparisons of the behaviour of the sample used immediately after purification were made with a sample that had been stored for several months and again after the same sample has been dried ($CaCl_2$) and redistilled. Further, samples from different sources were compared. In no case was there any evidence that the nature of the sample had any effect on the reaction rate.

Propene, for the inhibition studies, was prepared as in Part II (*loc. cit.*).

The apparatus and technique used were in essence the same as those described in Part I (*loc. cit.*). The rate of decomposition was measured by observing the rate of pressure increase, after having demonstrated that the percentage decomposition obtained from pressure measurements agreed with that calculated from the hydrobromic acid present, as determined by titration. Fig. 1 shows that the agreement between these two methods is very good. These observations imply that the reaction is well represented by $C_3H_7Br \longrightarrow C_3H_6 + HBr$, and that side reactions are present, if at all, only to a negligible extent. Further evidence comes from the fact that the products of reaction were completely and rapidly absorbed by bromine water, and were completely condensable in liquid air. These observations show that no saturated light hydrocarbons or hydrogen is formed during the reaction.

It was found that traces of oxygen exerted a powerful catalytic effect on the decomposition, and so it was essential not to allow oxygen to enter the reaction vessel. This was achieved by filling the reaction system between runs with oxygen-free nitrogen, which had been washed by bubbling through Fieser's solution to remove the last traces of oxygen. Nitrogen thus treated was examined in a mass spectrometer and no trace of oxygen was found.‡ The following Table shows the type of irreproducibility that was encountered before the nitrogen-flushing technique was developed. The rate coefficients, referring to 324°, are of first order, for reasons that will

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* Parts I and II, preceding papers.

† A preliminary account of this work appeared in *J. Chem. Phys.*, 1951, **19**, 977.

‡ The authors are indebted to Dr. C. A. Bunton for this test.

appear later. These are to be compared with the average value of 1·00 × 10^{-4} sec.$^{-1}$ obtained for the non-catalysed reaction.

p_0 (mm.)	212	250	238	218	164	285
10^4k_1 (sec.$^{-1}$)	2·80	2·89	5·37	3·76	6·44	6·67

The reaction was also catalysed by clean Pyrex surfaces, but as has been reported in other studies of the pyrolysis of organic halides, the gradual decomposition of the reaction products deposits a fine carbonaceous film which effectively eliminates the catalytic action. In the present reaction, the formation of an effective coating by this method took a considerable time. In a series of experiments starting with a clean reaction vessel, the rate constants showed a gradual decrease to a constant value when the wall effect had been effectively eliminated by the carbon coating.

As has been shown in Part I, the pyrolysis of allyl bromide leads to a relatively heavy carbonaceous coating on the walls of the vessel, so the reaction vessels were seasoned efficiently and rapidly by utilising this fact (see Part II, p. 975). Further, a reaction vessel which had been coated by prolonged contact with propene and hydrogen bromide, and which gave reproducible rate constants, was treated with allyl bromide; the reaction rates remained unaltered, and hence the coating produced by allyl bromide had no direct effect on the seasoned rate. In the following Table, which relates to $T = 341°$, the rate constants for a number of different

FIG. 1

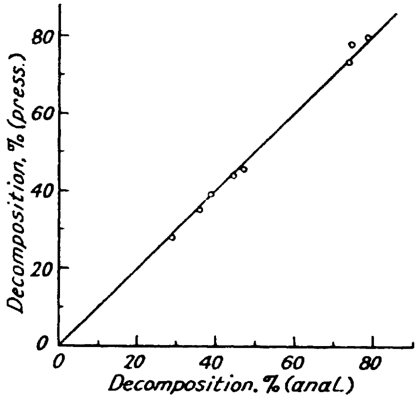


FIG. 2.

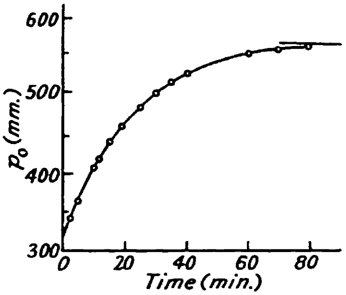


FIG. 1. *The percentage decomposition calculated from measurements of total pressure as a function of the percentage decomposition determined analytically.*

FIG. 2. *The variation of the total pressure of decomposing* iso*propyl bromide with time.*

Surface of vessel	Clean	Seasoned by products	Seasoned by allyl bromide
10^4k_1	15·3, 14·9	4·16, 4·17	4·00, 4·30

conditions of seasoning are shown. If air or oxygen was admitted into the vessel between runs, the coating was removed by oxidation.

The order of the reaction was shown to be unity by working in seasoned vessels in the absence of oxygen. Fig. 2 shows a typical pressure–time curve, and Fig. 3, curve (*a*), a typical log plot. It will be noted in Fig. 2 that the pressure increase is only about 90% of that to be expected. The interpretation of this in terms of an equilibrium will be discussed later. Again in Fig. 3, it will be seen that the first-order plot departs from linearity after about 30% reaction. This may also be interpreted in terms of an equilibrium between *iso*propyl bromide and propene and hydrogen bromide. For this reason, only the initial reaction rate has been determined.

In order to test the homogeneity of the reaction, a series of runs were done in a vessel, the surface : volume ratio of which had been increased by a factor of three over that of the unpacked vessel. The packed vessel was seasoned with allyl bromide. The results obtained are shown below. It may be concluded that the reaction is essentially homogeneous.

Temp.	10^4k_1, sec.$^{-1}$ (packed)	10^4k_1, sec.$^{-1}$ (unpacked)	k_1 packed/ k_1 unpacked	Temp.	10^4k_1, sec.$^{-1}$ (packed)	10^4k_1, sec.$^{-1}$ (unpacked)	k_1 packed/ k_1 unpacked
320°	1·00	1·00	1·00	335°	3·24	2·79	1·16
330	2·05	1·95	1·05	345	5·52	5·19	1·06
335	3·01	2·79	1·08	345	5·39	5·19	1·04

Kinetic Results.—The velocity constants obtained in the pressure range 200—450 mm. and temperature range 310—350° are set out below. As it was not convenient always to work at a given temperature, the velocity constants corrected to some convenient temperature within the range by means of the Arrhenius equation are shown. The results may be represented

Temp.	312°	319°	329°	341°	347°
No. of runs	5	3	8	8	4
10^5k_1, sec.$^{-1}$	5·92	9·56	18·0	40·4	58·3

by the Arrhenius equation

$$k = 4{\cdot}17 \times 10^{13} \exp(-47{,}800/\boldsymbol{R}T)(\text{sec.}^{-1})$$

and the plot of log k against T^{-1} is shown in Fig. 4.

FIG. 3.

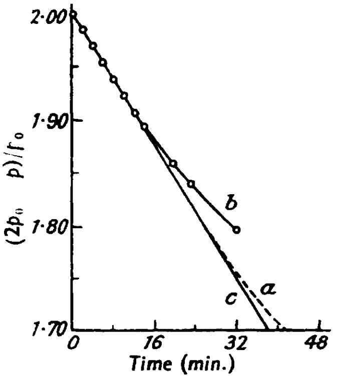


FIG. 4.

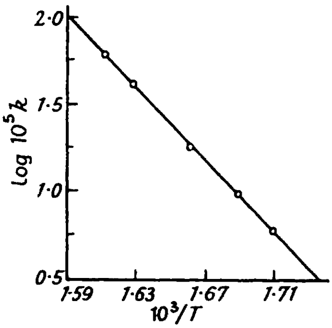


FIG. 3. *The effect of added propene upon the falling away from the first-order law*: (a) *in the absence of propene,* (b) *in the presence of 240 mm. of propene,* (c) *theoretical first-order plot in the absence of reverse reaction.*

FIG. 4. *The Arrhenius plot.*

To test further the invariance of the rate constant with pressure, the pressure range 30—120 mm. was covered, the results being shown below, where k_1 is in sec.$^{-1}$. The values of k_1 have been corrected to 327°. The low-pressure value, $1{\cdot}58 \times 10^{-4}$ sec.$^{-1}$ is to be compared with the

Temp.	p_0 (mm.)	10^4k_1	$(10^4k_1)_{\text{corr.}}$	Temp.	p_0 (mm.)	10^4k_1	$(10^4k_1)_{\text{corr.}}$
326·5°	116	1·48	1·55	329·5°	28·5	1·69	1·53
327·5	72	1·79	1·76	328·5	27·5	1·66	1·55
328·5	42·5	1·62	1·52			Mean	1·58

value obtained from the Arrhenius equation, namely, $1{\cdot}62 \times 10^{-4}$ sec.$^{-1}$. The good agreement is to some extent fortuitous, since the experimental error tends to be greater at lower initial pressures. It can be concluded that there is no evidence for any decrease in the rate down to 30 mm.

A number of runs were done in the presence of about 250 mm. of added propene (p_i). The velocity constants are shown below, k_1 being in sec.$^{-1}$. The mean values at 327° and 335° are to be compared with the values obtained from the Arrhenius equation, namely, $1{\cdot}64 \times 10^{-4}$ and $2{\cdot}79 \times 10^{-4}$ (sec.$^{-1}$). The reaction is thus clearly not affected by the presence of propene.

$T_c = 327°$					$T_c = 335°$				
Temp.	p_0 (mm.)	p_i (mm.)	10^4k_1	$(10^4k_1)_{\text{corr.}}$	Temp.	p_0 (mm.)	p_i (mm.)	10^4k_1	$(10^4k_1)_{\text{corr.}}$
327°	248	241	1·62	1·62	335°	244	252	2·81	2·81
328	283	237	1·77	1·66	336	246	244	2·96	2·88
327·5	242	233	1·72	1·67				Mean	2·84
			Mean	1·65					

Fig. 3 illustrates the earlier fall-off in the first-order plot for a run carried out in the presence of propene.

Experiments done in the presence of added bromine showed no very marked increase in the rate. Thus with about 2% of bromine, the initial fractional rate of pressure increase was about 30% greater than in the absence of bromine. Further, after 20% reaction there was no visible trace of bromine in the condensed contents of the reaction system.

Since allyl bromide had been used for seasoning the reaction vessel, it was thought desirable to determine the rate in the presence of a small amount of allyl bromide, but no alteration of the rate constant was observed.

Discussion

The pyrolysis of *iso*propyl bromide in a seasoned vessel has been shown to be a homogeneous first-order reaction yielding propene and hydrogen bromide. The rate constants are very reproducible, the same results having been recorded with different samples of material and over an extended period of time. In the pressure range studied, 25—450 mm., there is no evidence for a decrease in the rate constants. However, the first-order constants fall during the course of a run and this phenomenon is accentuated in the presence of added propene. Further, the initial rate constants are the same in the presence of propene.

The fall in the first-order constants during the course of a run, the fact that the ratio of final to initial pressure is less than 2 and the enhanced fall-off in the constants in the presence of propene can all be explained in terms of an equilibrium $C_3H_7Br \rightleftharpoons C_3H_6 +$ HBr lying well to the right. This equilibrium has not been investigated in detail because of the difficulty of correcting for dead space in the apparatus and because the equilibrium must be complex as C_3H_7Br represents either *n*- or *iso*-propyl bromide. Further evidence for the equilibrium is afforded by the lack of evidence for side reactions.

Three possible mechanisms exist for the decompositions of *iso*propyl bromide. In the first place the initial step may be the breaking of the C–Br bond

$$C_3H_7\text{–}Br \longrightarrow C_3H_7 + Br$$

followed by a non-chain radical mechanism such as has been postulated by Daniels for ethyl bromide or by one of us for allyl bromide. Such a mechanism might be

$$\begin{aligned} C_3H_7Br &\longrightarrow C_3H_7 + Br \\ Br + C_3H_7Br &\longrightarrow HBr + C_3H_6Br \\ C_3H_6Br + C_3H_7 &\longrightarrow C_3H_9Br + C_3H_6 \end{aligned}$$

in which case the overall activation energy of the process would be the C–Br bond dissociation energy. As this is most certainly greater than 47·8 kcal. this mechanism can be dismissed.

The second possible mechanism by analogy with *n*-propyl bromide is the Br chain reaction. To fit the first-order law, a mechanism somewhat different from that for *n*-propyl bromide must be considered; a possibility is

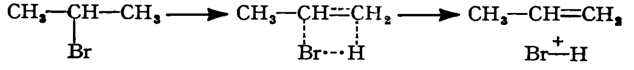
$$\begin{aligned} C_3H_7Br &\xrightarrow{k_1} C_3H_7 + Br \\ Br + C_3H_7Br &\xrightarrow{k_2} C_3H_6Br + HBr \\ C_3H_6Br &\xrightarrow{k_3} C_3H_6 + Br \\ Br + C_3H_6Br &\xrightarrow{k_7} \text{end of chain} \end{aligned}$$

This would lead to the overall rate constant $k = (k_1k_2k_3/k_7)^{\frac{1}{2}}$ and activation energy $E = \frac{1}{2}(E_1 + E_2 + E_3 - E_7)$. Such a mechanism should be powerfully inhibited by propene by competition between (2) and

$$Br + C_3H_6 \longrightarrow HBr + C_3H_5$$

No such inhibition is observed.

The remaining possibility is the direct unimolecular split through a four-centre transition state



$$CH_3\text{—}\underset{\displaystyle Br}{CH}\text{—}CH_3 \longrightarrow CH_3\text{—}\underset{\displaystyle Br\cdots}{CH}\text{=}\underset{\displaystyle H}{CH_2} \longrightarrow CH_3\text{—}CH\text{=}CH_2 \quad Br\overset{+}{\text{—}}H$$

Such a process is consistent with all the known facts. It would explain the clean nature of the reaction and the inability of propene to inhibit it. No satisfactory *a priori* estimation can be made of the activation energy for such a process : all that can be said is that the value 47·8 kcal. is not unreasonable. Such a mechanism has in fact been postulated by Kistiakowsky and Stauffer (*J. Amer. Chem. Soc.*, 1937, **59**, 165) for the decomposition of *tert.*-butyl bromide.

It might be argued that the catalytic effect of oxygen is evidence against the suggested mechanism. This is quite marked, as is shown in Fig. 5, which gives the pressure–time curves for a normal run and for one in the presence of about 0·1 mm. of oxygen. It does seem possible, however, that the oxygen effect produces long chains which may effectively swamp the normal elimination of hydrogen bromide. To test this view, the reaction was carried out in the presence of a trace of oxygen and added propene. The oxygen effect appeared at first to be inhibited, but then the rate of reaction slowly increased, giving rise to a sigmoid-type pressure–time curve. The catalysis produced by oxygen is far too marked to be merely due to oxidation of the carbonaceous film, thus exposing a clean surface. No extensive investigation of the oxygen effect has been attempted in the present work.

An interesting outcome of this work is the marked difference of mechanism in the pyrolysis of *n*- and *iso*-propyl bromide. In Part II it was shown that *n*-propyl bromide decomposes by a chain mechanism in which the initiation and propagation steps are:

$$\begin{aligned} n\text{-}C_3H_7Br &\longrightarrow C_3H_7 + Br \\ Br + C_3H_7Br &\longrightarrow HBr + C_3H_6Br \\ C_3H_6Br &\longrightarrow C_3H_6 + Br \end{aligned}$$

*iso*Propyl bromide on the other hand decomposes by the direct splitting out of hydrogen bromide. The difference in behaviour in these two cases can be explained by a more detailed examination of the steps in the chain mechanism postulated in Part II.

$$\begin{aligned} C_3H_7Br &\xrightarrow{k_1} C_3H_7 + Br \\ Br + CH_3\cdot CH_2\cdot CH_2Br &\xrightarrow{k_2} CH_3\cdot CH\cdot CH_2\cdot Br + HBr \\ &\xrightarrow{k_2'} CH_2\cdot CH_2\cdot CH_2\cdot Br + HBr \\ CH_3\cdot CH\cdot CH_2Br &\xrightarrow{k_3} CH_3\cdot CH{:}CH_2 + Br \\ CH_2\cdot CH_2\cdot CH_2Br + C_3H_7Br &\xrightarrow{k_4} CH_3\cdot CH\cdot CH_2Br + C_3H_7Br \\ CH_2\cdot CH_2\cdot CH_2Br + Br &\xrightarrow{k_5} Br\cdot CH_2\cdot CH_2\cdot CH_2Br \end{aligned}$$

The reaction of order 1·5 can be explained in terms of the facile decomposition of propagating (P) radicals ($CH_3\cdot CH\cdot CH_2Br$) and the condition $8k'_2k_4[C_3H_7Br] \gg k_1k_5$. This condition is readily seen to be satisfied at ordinary pressures. In the case of *n*-propyl bromide the initial Br-atom attack to give a P radical is on a secondary hydrogen atom whereas that to give a stopping radical is on a primary hydrogen atom hence $k_2^N > k_2'^N$ *. Also the radical-exchange reaction will be facilitated by the replacement of a secondary C–H bond by a primary one. However, with *iso*propyl bromide $k_2'^S > k_2^S$, and also $k_4^S \ll k_4^N$. Further, as will be seen later, $k_3^S \ll k_3^N$ and so all factors are in favour of a chain mechanism for *n*-propyl bromide. Finally, the unimolecular rate for *iso*propyl bromide is about 200 times greater than for *n*-propyl bromide (Green, Harden, Thomas, and Maccoll, *J. Chem. Phys.*, 1953, **21**, 178), which would further tend to favour the unimolecular mechanism.

Estimates of the C–Br bond dissociation energies in *n*- and *iso*-propyl bromides have recently been given by Linnett (*Proc. Roy. Soc.*, 1952, **216**, *A*, 361) as 67·9 and 67·6 kcal., respectively. On the assumption, which will also underlie subsequent arguments, that the pre-exponential terms in the expression for the rate constants of analogous steps are not greatly different, these values would imply $k_1^N \sim k_1^S$.

Van Artsdalen *et al.* (*J. Chem. Phys.*, 1944, **12**, 479; 1954, **22**, 28) have observed the

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* The superscripts N and S refer to *n*- and *iso*-propyl bromide, respectively.

rate of bromine-atom attack on primary and tertiary C–H bonds. The reported activation energies are

$$\mathrm{Br} + \mathrm{C_2H_6} = \mathrm{C_2H_5} + \mathrm{HBr};\ E = 13{\cdot}3\ \text{kcal.}$$
$$\mathrm{Br} + iso\text{-}\mathrm{C_4H_{10}} = \mathrm{C_4H_9} + \mathrm{HBr};\ E = 11{\cdot}4\ \text{kcal.}$$

These values would suggest that for *n*- and *iso*-propyl bromide

$$E_2^{\mathrm{N}} - E_2'^{\mathrm{N}} \sim 1\ \text{kcal.}:\ E_2'^{\mathrm{S}} - E_2^{\mathrm{S}} \sim 1\ \text{kcal.}$$

At the relevant temperature, the 1 kcal. difference in activation energy would lead to a factor of about 3 in the rate.

FIG. 5.

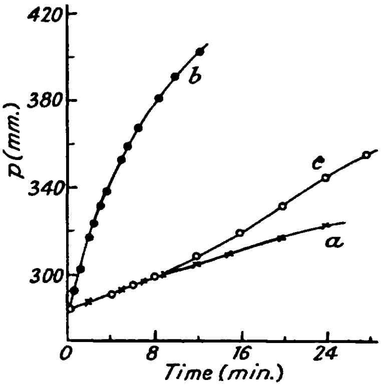


FIG. 6.

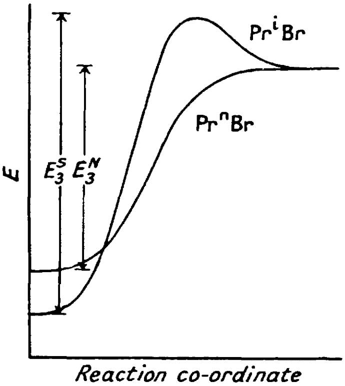


FIG. 5. *The rate of decomposition of* iso*propyl bromide* (a) *in the absence of oxygen,* (b) *in the presence of* ~0·1 *mm. of oxygen, and* (c) *in the presence of* ~0·1 *mm. oxygen and* 120 *mm. of propene.*

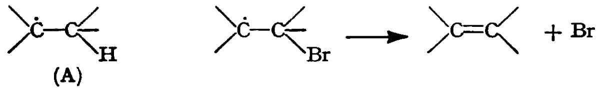
FIG. 6. *The activation energies for bromoalkyl-radical decomposition.*

Information relating to the radical-exchange reaction comes from the work of Trotman-Dickenson and Steacie, reported by the former author (*Discuss. Faraday Soc.*, 1951, **10**, 112). The activation energies for methyl-radical attack upon primary and secondary C–H bonds are respectively 10·2 and 8·2 kcal. This would suggest that $k_4^{\mathrm{N}} \sim 10k_4^{\mathrm{S}}$ in the temperature range experimentally investigated.

An estimate of the stability of the bromoalkyl radical can be obtained by thermochemical arguments analogous to those used by Szwarc (*ibid.*, p. 144) in his discussions of the C–H bond dissociation energies in radicals of the type (A). He used the equation

$$D(\text{M–H}) = \Delta H_f(\text{H}) + \Delta H_f(\text{M}) - \Delta H_f(\text{M–H})$$

where M–H represents the radical formed by the addition of a hydrogen atom to the olefin M and ΔH_f(A) is the enthalpy of formation of A. Provided ΔH_f(Br–M) can be estimated, a lower limit for the activation energy of the reaction



can be obtained by this method. The enthalpies of formation of the bromoalkyl radicals can be obtained by use of the equation

$$\Delta H_f(\text{M–Br}) = D(\text{Br–M–H}) + \Delta H_f(\text{Br–M–H}) - \Delta H_f(\text{H})$$

if it is assumed that the C–H bond dissociation energy is the same in the alkyl bromide (Br–M–H) as in the unsubstituted hydrocarbon. The values used for *D*(C–H) are taken from the work of Stevenson as quoted by Evans (*ibid.*, p. 1) and are 97 kcal. for a primary C–H bond and 94 for a secondary. From the known values of the enthalpies of formation of *n*- and *iso*-propyl bromide, –18·7 and –23·8 kcal., respectively (Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220), the values 23·3 and 21·2 kcal. can be calculated for the ΔH_f of $CH_3{\cdot}\dot{C}H{\cdot}CH_2Br$ and $CH_3{\cdot}CHBr{\cdot}\dot{C}H_2$, respectively. Applying now the equation

$$D(\text{M–Br}) = \Delta H_f(\text{Br}) + \Delta H_f(\text{M}) - \Delta H_f(\text{M–Br})$$

and using the value 4·9 kcal. for ΔH_f(propene) (Selected Values of the Properties of Hydrocarbons, Nat. Bureau of Standards, Washington) we find the M–Br bond dissociation energies for the above two radicals to be 8·3 and 10·4 kcal., respectively. In order to estimate the activation energies for the C–Br splitting, account has to be taken of the activation energy associated with the steps

$$CH_3{\cdot}CH{:}CH_2 + Br \longrightarrow CH_3{\cdot}CH{\cdot}CH_2Br$$
$$CH_3{\cdot}CH{:}CH_2 + Br \longrightarrow CH_3{\cdot}CHBr{\cdot}CH_2$$

Indirect evidence relating to these reactions comes from a study of the photo-addition of hydrogen bromide to olefins investigated by Vaughan, Rust, and Evans (*J. Org. Chem.*, 1942, **7**, 477). This reaction probably proceeds by the mechanism

$$HBr \xrightarrow{h\nu} H + Br$$
$$Br + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}CH_2Br$$
$$CH_3{\cdot}\dot{C}H{\cdot}CH_2Br + HBr \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2Br + Br$$

together with some chain-ending step. These authors found that in all cases the addition was exclusively abnormal in the Kharasch sense, which implies that the rate of bromine addition to the 1-position in propene vastly exceeds that to the 2-position. The equilibrium and kinetic behaviour are shown in Fig. 6, in which the reaction path is sketched in each case. It may be concluded from these arguments that $k_3^{N} \gg k_3^{S}$. This factor is possibly the most important in explaining the difference in behaviour between *n*- and *iso*-propyl bromide on pyrolysis, because if k_3^{S} is small, the chain mechanism will not be available to *iso*propyl bromide.

It is of interest to enquire as to the relevance to the bromides of the rules suggested by Barton *et al.* (*Trans. Faraday Soc.*, 1949, **45**, 725; *J.*, 1951, 2039) correlating mechanism and structure in the case of the chlorides. These authors have suggested that a chain mechanism will only obtain if neither the decomposing chloride nor the products of decomposition are inhibitors for the chain mechanism. Inhibition by the reactant is explained in terms of the nature of the radical produced by chlorine-atom attack upon the reactant. Thus whereas in 1 : 2-dichloroethane the radical $\dot{C}H{\cdot}Cl{\cdot}CH_2Cl$ is produced; in the case of the 1 : 1-dichloroethane the radical $CH_3{\cdot}\dot{C}Cl_2$ is formed. In the former case the product is a P radical, in the latter an S radical. Thus the 1 : 1-dichloroethane molecule is an inhibitor for its own chain decomposition. Neither of these rules appears to hold in the case of the bromides, for both 1 : 1- and 1 : 2-dibromoethane decompose normally by a chain mechanism (P. T. Good, unpublished work), and further, all primary bromides so far investigated have been shown to decompose partially by a chain mechanism, even though an olefinic inhibitor is one of the products of reaction. The explanation of the difference in behaviour is at least in part forthcoming, namely, in the first case the possibility of conversion of an S radical into a P radical, and in the second, the relative inefficiency of straight-chain olefins as inhibitors (P. J. Thomas, unpublished work). It is hoped in later communications to deal with the question of the chain mechanism in greater detail.

It remains to discuss the observed ratio of final to initial pressure (<2), the fall in rate constant as the reaction proceeds, and the enhanced fall in the presence of added propene. All these facts are consistent with the existence of an equilibrium $C_3H_7Br \rightleftharpoons C_3H_8 + HBr$. Reference to Fig. 1 shows that when, for example, 80% of the *iso*propyl bromide has reacted as determined by pressure measurements, 80% of the hydrogen bromide has been eliminated. This implies that the low value of the ratio of final to initial pressure cannot be due to any extensive polymerisation of the propene. Further, if the rate of reaction is given by

$$-\,d[C_3H_7Br]/dt = k_1[C_3H_7Br] - k_2[C_3H_6][HBr]$$

then, while the initial rates give a true measure of k_1, the log plots will be concave upwards and the departure from a straight line will be greater the higher the initial pressure and the higher the pressure of added propene.

The present technique was not considered suitable for investigating the equilibrium, because of dead-space errors. Thus, although the volume of the dead space was too small to account for the fact that only 80% of the bromide decomposes, it is considered that such an effect operates to an extent which would render any quantitative study of equilibrium of doubtful value.

Blades and Murphy (*J. Amer. Chem. Soc.*, 1952, **74**, 6219) have reported an investigation of the pyrolysis of *iso*propyl bromide using a flow system, with Szwarc's toluene-carrier gas technique (*J. Chem. Phys.*, 1949, **17**, 432). These authors covered a temperature range some 150° higher than that covered in the present work and arrived at a rate expression

$$k = 4{\cdot}0 \times 10^{13} \exp(-47{,}700/\boldsymbol{R}T)$$

in very good agreement with the values reported here. As might have been expected from the reported absence of a free-radical mechanism in this reaction (*ibid.*, 1951, **19**, 977), Blades and Murphy could detect no dibenzyl in their reaction products. This compound would have been produced by the steps

$$C_3H_7Br \longrightarrow C_3H_7 + Br \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$
$$Br + CH_3Ph \longrightarrow CH_2Ph + HBr \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$
$$C_3H_7 \longrightarrow C_3H_6 + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$
$$H + CH_3Ph \longrightarrow CH_2Ph + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$
$$2CH_2Ph \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2{\cdot}Ph \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

Reaction (1), as explained on p. 983, would have an activation energy of about 676 kcal., the rate being reasonably expressed as $k = 10^{13} \exp(-67{,}600/\boldsymbol{R}T)$. This process would thus be completely insignificant compared with the unimolecular elimination of hydrogen bromide. It could thus be confidently predicted that any inert carrier gas would have been sufficient in the flow investigation.

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