1005. *Studies in the Pyrolysis of Organic Bromides. Part VIII.* Pyrolysis of* tert.-*Amyl Bromide.*

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tert.-Amyl bromide decomposes in the range 220—270° according to a first-order rate law, to give hydrogen bromide and an olefin, which infrared studies indicate is 2-methylbut-2-ene. *cyclo*Hexene has no effect on the rate, and relatively large pressures of bromine cause only a slight acceleration. In seasoned reaction vessels the reaction is homogeneous. The rate is given by $k_1 = 3.98 \times 10^{13}$ exp $(-40,500/RT)$ sec.$^{-1}$) and it is concluded that the decomposition occurs by unimolecular elimination of hydrogen bromide.

IN studies designed to correlate the gas-phase mechanism of decomposition of organic bromides with molecular structure, Maccoll *et al.* (Parts I—VI [1]) have so far established three different homogeneous mechanisms for the pyrolysis of alkyl bromides. (1) Allyl bromide decomposes by a radical, non-chain process (Part I), as a result of rupture of the C–Br bond; (2) *n*-propyl bromide decomposes by a bromine-atom chain mechanism (Part II); (3) *iso*propyl (Part III), *sec.*-butyl (Part IV), *cyclo*hexyl (Part V), and *tert.*-butyl bromide (Part VI) decompose in seasoned vessels by unimolecular elimination of hydrogen bromide. The present investigation was undertaken to determine the effect of replacing a primary C–H bond (cf. *tert.*-butyl bromide) by a secondary one, on the rate of elimination of hydrogen bromide. No physicochemical studies of the kinetics of the pyrolysis of *tert.*-amyl bromide have been reported hitherto.

EXPERIMENTAL

The apparatus employed was essentially that described in Part I.[1] *tert.*-Amyl bromide was introduced from a vapour reservoir. Reaction vessels were seasoned by the pyrolysis products of allyl bromide.

tert.-Amyl bromide, prepared from pure *tert.*-amyl alcohol by Bryce-Smith and Howlett's method,[2] was fractionally distilled, and collected at 48·8°/100 mm. The refractive index was n_D^{25} 1·4392 (cf. 1·4421 reported by Brown and Stern [3]).

The rate of decomposition was measured by following the rate of pressure change on the basis of the equation $C_5H_{11}Br \longrightarrow C_5H_{10} + HBr$. Because of the rapid recombination of the products of reaction during condensation, it was not possible to compare rate constants calculated from the pressure increase with those derived from the hydrogen bromide produced (cf. *tert.*-butyl bromide, Part VI). However, circumstantial evidence confirms the stoicheiometry of the reaction. Thus a series of runs was followed until no further increase in pressure was detectable. In all cases the final pressure (p_t) reached a value nearly double the initial pressure (p_0) as shown in Table 1.

TABLE 1. *Ratio of final to initial pressure.*

Temp.	269·4°	269·4°	269·4° *	263·3°	254·1°	247·7°	242·3°	242·3°	242·3°	235·6°	233·1°
p_0 (mm.) ...	257	203	189	199	252	209	272	269	136	272	266
p_t/p_0	1·85	1·90	1·83	1·81	1·85	1·86	1·83	1·80	1·90	1·76	1·69

* In the presence of 57 mm. of *cyclo*hexene.

According to the proposed scheme, p_t/p_0 should reach a value of 2. The fact that this ratio is always less than 2 is attributed to two factors. (*a*) An equilibrium may occur between *tert.*-amyl bromide and its decomposition products; this would be in keeping with the behaviour of

* Part VII, preceding paper.

[1] Maccoll *et al.*, *J.*, 1955, 965 (Part I), 973 (Part II), 979 (Part III), 2445 (Part IV), 2449 (Part V), 2454 (Part VI).
[2] Bryce-Smith and Howlett, *J.*, 1951, 1141.
[3] Brown and Stern, *J. Amer. Chem. Soc.*, 1950, **72**, 5068.

the bromides already investigated, in particular with that of *tert.*-butyl bromide (Part VI; [1] Kistiakowsky and Stauffer [4]). (*b*) In the apparatus used, the dead-space effect will be of some importance; the difficulty of estimating this effect quantitatively prevented precise investigation of the equilibrium. Further evidence of the stoicheiometry is that no uncondensable gases were formed even in long runs at high temperatures.

The olefin C_5H_{10} may be 2-methylbut-2- or -1-ene. Recombination was so rapid that the olefin could not be separated from the hydrogen bromide, but the olefin was identified as 2-methylbut-2-ene by infrared analysis of the hot reaction mixture in the range 10—13·5 μ.* In the Figure the spectrum of the reaction mixture in the given wavelength range is compared with that of 2-methylbut-2-ene. It is possible that a small amount of 2-methylbut-1-ene is also formed.

Addition of hydrogen bromide to either 2-methylbut-2- or -1-ene under the conditions used here would give *tert.*-amyl bromide, according to Markownikow's rule. It is of interest that if

Infrared spectrum of the products of pyrolysis of tert.-*amyl bromide.*

(*a, c*) *Reaction products.*
(*b*) *Pure 2-methylbut-2-ene.*
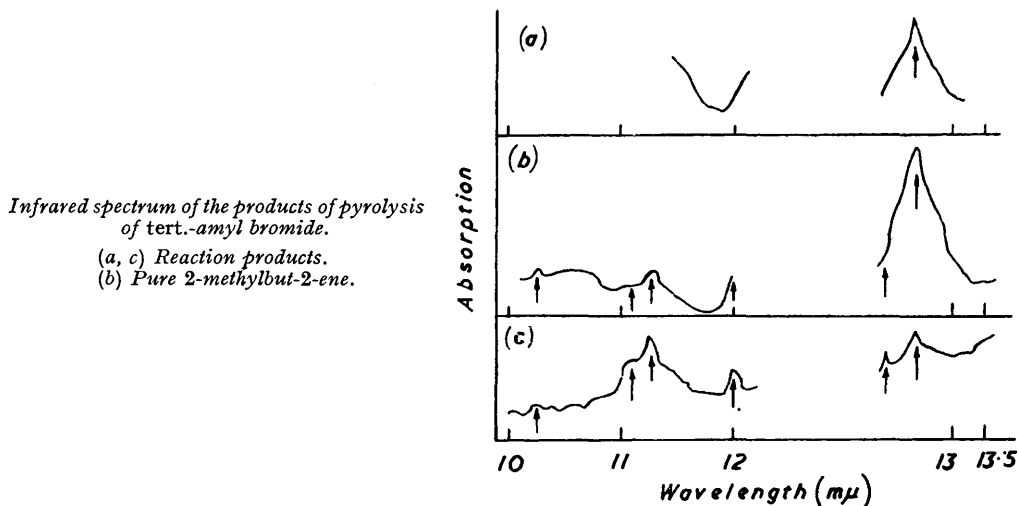
the reaction is stopped by condensing the products, and then re-started, both the original initial pressure and the original rate of decomposition are approximately reproduced. Table 2 shows the results of two such runs.

TABLE 2. *The effect of re-starting a run.*

Temp.	p_0 (mm.)	$10^4 k_1$ (sec.$^{-1}$)	p_t (mm.)	p_0'	$10^4 k_1'$ (sec.$^{-1}$)
247·7°	252	5·67	385·5	257	5·37
247·7	241	6·13	380·5	254	6·08

It was also found that when a mixture of approximately equal pressures of 2-methylbut-2-ene and hydrogen bromide was admitted to the reaction vessel and then condensed out and readmitted, a marked decrease in pressure occurred, followed by a gradual increase. The rate of decomposition of the bromide was then calculated by assuming the decrease to be due to addition and the increase to decomposition of the bromide formed. The first-order rate plot led to an initial rate of 7·18 × 10^{-4} sec.$^{-1}$, close to the rate calculated from the Arrhenius plot (7·41 × 10^{-4} sec.$^{-1}$).

A series of runs with varying initial pressures was carried out in order to verify the order of the reaction. The results are in Table 3. Graphs were drawn for reactions of order 0·5, 1, and 1·5, and in all cases the first and third of these were markedly curved, whereas the first-order plots were linear up to about 40% reaction. Further, as can be seen in Table 3, the first-order

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* The author is indebted to Mr. D. W. Watson for assistance with the infrared analysis.

[4] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.

constants did not vary significantly over a five-fold range of initial pressure. It may be concluded that the reaction is of the first order. The fact that the first-order constants begin

TABLE 3. *The pressure dependence of the velocity constants.*

p_0 (mm.)	364	352	296	290	252	241	224·5	217·5	209	121	79·2
$10^4 k_1$ (sec.$^{-1}$)	6·12	5·92	5·87	6·22	5·67	6·13	6·19	5·68	6·13	5·80	6·17

to fall in the later stages of the reaction is a direct consequence of the failure of the ratio p_t/p_0 to reach 2.

The temperature range 220—270° was next systematically explored. As Table 3 indicates the characteristic range of variation of rate constants obtained, it is unnecessary to report all the results in detail: Table 4 summarises the experimental results.

TABLE 4. *The temperature dependence of the velocity constant.*

Temp.	223·4°	233·1°	235·6°	242·3°	247·7°	254·1°	263·3°	269·4°
No. of runs	11	11	9	12	11	11	11	10
$10^4 k_1$ (sec.$^{-1}$)	0·922	1·99	2·43	4·26	5·99	9·95	19·38	28·84

The Arrhenius plot yielded the rate equation

$$k_1 = 3·98 \times 10^{13} \exp (40,500/\mathbf{R}T) \text{ (sec.}^{-1})$$

The experimental points all lie close to the best straight line.

The effect of surface on the rate of decomposition was studied by means of runs in a vessel packed with thin-walled Pyrex tubing. The packed vessel had a surface : volume ratio 6·8 times that of the unpacked vessel and was seasoned by the products of pyrolysis of allyl bromide before use. The results (Table 5) show how small is the effect of an increase in surface area and it is concluded that the reaction is homogeneous.

TABLE 5. *Decompositions in a packed vessel.*

Temp.	237·6°	248·7°	260·7°
Mean $10^4 k_1$ (sec.$^{-1}$)	3·35 (3 runs)	6·86 (3 runs)	15·87 (6 runs)
Calc. $10^4 k_1$ (sec.$^{-1}$)	2·84	6·61	15·78

In order to identify the mechanism of the pyrolysis, a number of runs were carried out in the presence of added *cyclo*hexene. This substance has been shown [5] to inhibit the chain mode of decomposition of *n*-propyl bromide. The results are in Table 6, p_i being the pressure of added *cyclo*hexene. It is seen that the rate is independent of the *cyclo*hexene pressure. This provides strong evidence against a chain mechanism for the pyrolysis. Further, in the normal runs and also in those with added *cyclo*hexene no induction periods were apparent.

TABLE 6. *Effect of added* cyclohexene.

	At 223·4° k_1 (calc.) = 0·916 × 10^{-4} (sec.$^{-1}$)					At 269·4° k_1 (calc.) = 28·8 × 10^{-4} (sec.$^{-1}$)			
p_i (mm.)	0	48	49	71	88	90	0	55	57	120
p_0 (mm.)	—	207	195·5	210	203·5	213	—	108	189	191
$10^4 k_1$ (sec.$^{-1}$)	0·922 *	0·940	0·886	0·899	0·908	0·864	28·8 *	30·0	29·8	28·7

* Mean of 10 runs.

It has been shown (Part I) that allyl bromide decomposes by a mechanism involving a primary splitting off of a bromine atom. Further, Thomas (unpublished work) has shown that decomposing allyl bromide is capable of catalysing the decomposition of those normal bromides for which the uninhibited mode of decomposition involves, at least in part, bromine atom chains. In addition, Thomas has shown that decomposing allyl bromide is capable of stimulating a chain mechanism in some compounds that normally decompose by a unimolecular mechanism.

[5] Maccoll and Thomas, *J.*, 1957, 5033.

Similarly, molecular bromine, which thermally dissociates into bromine atoms, has been shown by Daniels and Veltman [6] to catalyse the decomposition of ethyl bromide. For these reasons, the decomposition of *tert.*-amyl bromide was investigated in the presence of both allyl bromide and bromine. The results are in Table 7, where p_s is the pressure of added stimulant. Allyl

TABLE 7. *Effects of allyl bromide and bromine as stimulants (at 254·1°).*

	Allyl bromide					Bromine		
p_s (mm.)	0	52	69	102	149	37	59	69
p_0 (mm.) [a]	—	236	210	230	227	232	164·5	101·5
$10^4 k_1$ (sec.$^{-1}$) [b] ...	9·95	9·72	10·2	10·0	9·89	9·89	10·2	11·6

[a] Mean of 11 runs. [b] $10^4 k_1$ (calc.) $= 9·75$ sec.$^{-1}$.

bromide appears to have little effect on the rate, whereas bromine at high pressures appears to catalyse it slightly. A quantitative study of the sensitised decomposition was not undertaken in the case of bromine since the sensitised reaction did not show good first-order behaviour, probably owing to side reactions between bromine and *tert.*-amyl bromide or the olefin.

The absence of induction periods, and the lack of inhibition by *cyclo*hexene, show that the mechanism of decomposition is unlikely to be a radical–atom chain process. The view is substantiated by the experiments with added allyl bromide and bromine. Further, the magnitude of the activation energy (40·5 kcal./mole) rules out the possibility of a radical non-chain process, since for such a mechanism, the activation energy must be of the order of the C–Br bond dissociation energy (∼64 kcal./mole). The fact that the reaction is homogeneous and of the first order, together with the evidence cited above, proves that the decomposition occurs by unimolecular elimination of hydrogen bromide. The similarity of the activation energy to that for *tert.*-butyl bromide (42·2 kcal./mole) (Part VI) confirms this.

That the major olefinic product is 2-methylbut-2-ene implies that the elimination of hydrogen is easier from CH than from CH_2, in line with the fact that decomposition of *tert.*-amyl bromide is 3·2 times faster than that of *tert.*-butyl bromide at 250°. This suggests that the maximum amount of 2-methylbut-1-ene in the products should be of the order of 20%. That the nature of the C–Br bond is the major factor determining the rate of elimination of hydrogen bromide has been stated before.[7] The present work shows that the nature of the C–H bond plays a rôle, albeit a minor one.

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[6] Daniels and Veltman, *J. Chem. Phys.*, 1937, **7**, 756.
[7] Green, Harden, Maccoll, and Thomas, *ibid.*, 1953, **21**, 170.