1006. *Studies in the Pyrolysis of Organic Bromides. Part IX.*[1] *The Pyrolysis of 2-Bromo-2 : 3-dimethylbutane.*

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Over the temperature range 210—260°, the pyrolysis of 2-bromo-2 : 3-dimethylbutane in seasoned vessels is a homogeneous, first-order reaction, the rate constant being $k_1 = 3{\cdot}47 \times 10^{13} \exp(-39{,}000/\boldsymbol{R}T)$ (sec.$^{-1}$). At the lower temperatures there may be a small contribution from a chain mechanism, but the predominant mechanism is the unimolecular elimination of hydrogen bromide. Some general conclusions are drawn as to the mode of decomposition of *tert.*-alkyl bromides.

PARTS VI and VIII [1] described the pyrolyses of *tert.*-butyl and *tert.*-amyl bromide. While the C–Br bond in both these compounds is tertiary, the C–H bond involved in the elimination of hydrogen bromide is primary in the former and secondary in the latter case. The ratio of the rates at 250° was 3·2. It is of interest to examine a case where the C–H bond is tertiary, the simplest example of such a compound being 2-bromo-2 : 3-dimethylbutane. There has not previously been a physicochemical study of the pyrolysis of this compound.

EXPERIMENTAL

According to Kishner,[2] the required bromide can be readily obtained from 2 : 3-dimethylbutan-2-ol by treatment with hydrogen bromide. Interaction of methylmagnesium iodide and methyl *iso*propyl ketone, extraction with ether, and distillation of the product gave 2 : 3-dimethylbut-2-ene, b. p. 72°. This was treated with excess of hydrogen bromide solution, and the organic layer collected, washed, and dried; distillation gave a bromide, b. p. 61·8—62·2°/72 mm., n_D^{25} 1·4500 (Krishner [2] reports 1·4501). A second sample, prepared from the alcohol by Bryce-Smith and Howlett's method [3] and fractionated, had b. p. 59·3°/62 mm., n_D^{25} 1·4497. The two samples showed identical kinetic behaviour.

For primary and secondary bromides investigated so far, the stoicheiometry of the decomposition has been shown accurately to be represented as:

$$C_nH_{2n+1}Br = C_nH_{2n} + HBr \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

However, for the tertiary bromides so far examined, it has not been possible to compare the amount of decomposition derived from pressure measurements with that derived by a direct titration of the acid produced because of the rapid re-addition which occurs during the condensing or vaporisation of the products. However, it is known that *tert.*-butyl and *tert.*-amyl bromides decompose according to equation (1) and that under the conditions of these experiments the olefins produced are *iso*butene and 2-methylbut-2-ene, respectively. With 2-bromo-2 : 3-dimethylbutane, a number of runs at temperatures from 222° to 257° and initial pressures from 100 to 200 mm. gave ratios of final to initial pressure in the range 1·80—1·90, to be compared with the value of 2 demanded by equation (1). Dead-space errors [4] and the reverse reaction suffice to explain the small discrepancy. Further, no gases uncondensable in liquid air (*e.g.*, hydrogen or methane) were detected in the products. Again, when the products were condensed out and then re-admitted to the reaction vessel, the pressure was observed to have fallen to a value intermediate between the initial value and the value at the time of condensation. From experiments of this type, the degree of recombination may be estimated. Thus at 229° and an initial pressure of 317 mm. the reaction was stopped when the pressure had risen to 475 mm.: the initial pressure on re-admission was 359 mm., corresponding to 73% of recombination. Another experiment gave 67% of recombination. It was further observed that the pressure–time curve obtained after re-admission was superimposable on the original curve, after a suitable change of origin. These observations confirm the suggested stoicheiometry.

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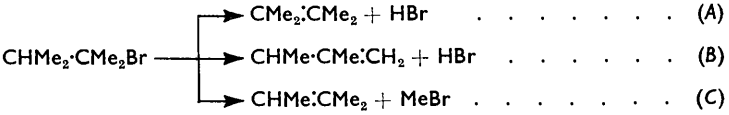
[1] Part VI, *J.*, 1955, 2454; Part VII and VIII, preceding papers.

[2] Kishner, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 165; *Chem. Zentr.*, 1912, **16**, *I*, 2025.

[3] Bryce-Smith and Howlett, *J.*, 1951, 1141.

[4] Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053.

Since no hydrogen or methane was formed in the pyrolysis, three possibilities remain:



$$\mathrm{CHMe_2{\cdot}CMe_2Br} \rightarrow \mathrm{CMe_2{:}CMe_2} + \mathrm{HBr} \quad \ldots\ldots\ (A)$$

$$\mathrm{CHMe_2{\cdot}CMe_2Br} \rightarrow \mathrm{CHMe{\cdot}CMe{:}CH_2} + \mathrm{HBr} \quad \ldots\ldots\ (B)$$

$$\mathrm{CHMe_2{\cdot}CMe_2Br} \rightarrow \mathrm{CHMe{:}CMe_2} + \mathrm{MeBr} \quad \ldots\ldots\ (C)$$

Reaction (*C*) is excluded because (i) elimination of methyl bromide has never been observed from alkyl bromides, and (ii) when approximately equal amounts of 2-methylbut-2-ene and methyl bromide were admitted to the reaction vessel, condensed out, and then re-admitted, no change in pressure occurred, in marked contrast with the behaviour of the reaction products. Hydrogen bromide is involved because when approximately equal pressures of hydrogen bromide and tetramethylethylene were vapourised into the reaction vessel, condensed out, and re-admitted, analysis of the changes of pressure yielded a rate constant $k_1 = 5{\cdot}50 \times 10^{-4}$ sec.$^{-1}$, to be compared with the value of $5{\cdot}86 \times 10^{-4}$ sec.$^{-1}$ calculated from the Arrhenius equation described below. A decision between reaction (*A*) and (*B*) can best be made on the basis of the kinetic behaviour. Production of 2 : 3-dimethylbut-1-ene would require fission of a tertiary C–Br and a primary C–H bond, so the rate should not markedly differ from that for *tert.*-butyl bromide; the observed rate is however, about eight times that of *tert.*-butyl bromide, indicating that scheme (*A*) represents the reaction.

The kinetic studies were carried out in a vessel seasoned by the products of the pyrolysis of allyl bromide. Pressure–time curves were obtained by the technique described previously, and velocity constants were derived from the expression, $p_t = 2p_0 - P_t$, where p_0 is the initial pressure of the bromide, p_t its pressure at time t, and P_t is the total pressure at time t. In all cases linearity was obtained in first-order plots up to about 50% decomposition. The invariance of the first-order rate constant with initial pressure is illustrated in Table 1: over an eight-fold variation of initial pressure the first-order rate constants do not vary significantly.

TABLE 1. *Pyrolyses at* 243·1°.

p_0 (mm.)	372	367	334	294	241	226·5	219	182	161	127·5	94·3	49·2
10^4k_1 (sec.$^{-1}$)	10·19	10·11	10·62	10·39	10·26	10·11	10·26	10·42	10·21	10·21	10·31	10·67

It was next established that the reaction was homogeneous. A packed and seasoned reaction vessel was used, the surface : volume ratio being about four times that of the unpacked vessel. Table 2 shows the results of such experiments; the calculated figure is obtained from the Arrhenius equation.

TABLE 2. *Runs in a packed vessel.*

Temp.	No. of runs	10^4k_1 (sec.$^{-1}$) (obs.)	10^4k_1 (sec.$^{-1}$) (calc.)	Temp.	No. of runs	10^4k_1 (sec.$^{-1}$) (obs.)	10^4k_1 (sec.$^{-1}$) (calc.)
252·5°	5	22·32	20·89	223·5°	4	2·64	2·34
243·4	3	10·84	10·62				

The variation of the velocity constant with temperature is illustrated in Table 3. The results fit the Arrhenius equation:

$$k_1 = 3{\cdot}47 \times 10^{13} \exp\left(-39{,}000/\boldsymbol{R}T\right) \text{ (sec.}^{-1}\text{)}$$

In order to test for the presence of reaction chains, runs were carried out in the presence of added *cyclo*hexene, shown by Maccoll and Thomas (following paper) to be a powerful inhibitor of the chain mode of pyrolysis of organic bromides. The results are in Table 4, where p_0 is the initial pressure of the bromide and p_i the pressure of *cyclo*hexene.

TABLE 3. *Effect of temperature.*

Temp.	256·6°	250·2°	243·1°	235·5°	229·0°	221·8°	213·0°
No. of runs	12	12	12	12	10	12	11
10^4k_1 (sec.$^{-1}$)	26·19	17·56	10·31	5·97	3·54	1·97	0·979

Although there is no effect due to *cyclo*hexene at 257°, there is a small but increasing effect as the temperature is lowered: at about 214° the reduction is of the order of 6%. This is barely within the experimental error but is believed to be significant, and suggested that a chain reaction may play a small part in the pyrolysis.

TABLE 4. *Effect of added* cyclo*hexene.*

	At 256·6°				At 243·1°			
p_i (mm.)	0	123	106	101	0	90	90	83
p_0 (mm.)	—	183·5	184	193	—	192	186	177
10^4k_1 (sec.$^{-1}$) ...	26·2 [a]	26·7	25·6	26·2	10·31 [a]	10·06	10·08	9·75

	At 214·4°					At 213·0°					
p_i (mm.)	0	57	56	51	50·5	0	229	113	93	60·5	32
p_0 (mm.)	—	153	188	104	170·5	—	167	234	193	108	94
10^4k_1 (sec.$^{-1}$) ...	1·13 [b]	1·10	1·03	1·05	1·09	0·98 [a]	0·92	0·88	0·98	0·80	0·92

[a] Mean of 12 runs. [b] Calc. from Arrhenius plot.

As a result, the effect of chain stimulants was investigated, *e.g.*, of allyl bromide and bromine. The latter has been shown to catalyse the pyrolysis of ethyl bromide [5] whereas the former has been shown by Thomas (unpublished work) both to catalyse the decomposition of those substances which normally decompose by a chain mechanism and to induce a chain mode of decomposition in certain others. In both cases, Thomas has shown that in the presence of an inhibitor such as *cyclo*hexene the catalysed rate is reduced to the normal value. The behaviour of 2-bromo-2 : 3-dimethylbutane under these conditions is shown in Table 5, p_s being the pressure of stimulant. It is concluded that the reaction can be catalysed by allyl bromide or bromine, and that the catalysis can be inhibited by addition of *cyclo*hexene.

TABLE 5. *Effect of stimulants* (*at* 235·5°).

	Allyl bromide						Bromine				
p_s (mm.)	0	33	57	95	23	35	0	40	71	37	39
p_i (mm.)	0	0	0	0	53	74	0	0	0	81	67
p_0 (mm.)	—	199	177	210	125	159	—	217	223	279	210
10^4k_1 (sec.$^{-1}$) ...	5·97 *	6·94	7·18	7·16	5·86	5·81	5·97 *	7·09	8·89	6·00	6·09

* Mean of 12 runs.

DISCUSSION

The main points that have emerged from the experimental study are: (1) 2-Bromo-2 : 3-dimethylbutane decomposes cleanly into 2 : 3-dimethylbut-2-ene (main product) and hydrogen bromide in the temperature range 213—257°. (2) The reaction is homogeneous and of the first order, over an initial pressure range of 50—400 mm. (3) Added *cyclo*hexene has only a barely significant effect on the rate and that only at the lower temperatures. (4) Added allyl bromide and bromine catalyse the decomposition, such catalysis being inhibited by the addition of *cyclo*hexene.

From these facts, it may be deduced that the predominant mechanism is a unimolecular elimination of hydrogen bromide, through a four-centre transition state. A radical non-chain mechanism,[1] such as that suggested by Daniels and Veltman,[5] is ruled out by the activation energy required, which is the C–Br bond dissociation energy (60 kcal./mole). This is in keeping with the observed behaviour of the other tertiary bromides studied.[1] However there is an additional feature of the pyrolysis of the present compound, namely, its capacity to support a chain mode of decomposition in favourable circumstances. Now with *iso*propyl bromide there is no evidence of a chain mechanism, but with *sec.*-butyl bromide at the lower temperatures there appears to be a small contribution by a chain mechanism. It appears that a very significant factor in the facilitating of a chain

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[5] Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 756.

mode of pyrolysis is the presence of a weakened C–H bond, which conceivably reduces the activation energy of attack by a bromine atom on the present bromide:

$$\mathrm{Br} + \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{Br} \longrightarrow \cdot\mathrm{C}_n\mathrm{H}_{2n}\mathrm{Br} + \mathrm{HBr} \qquad . \; . \; . \; . \; . \qquad (2)$$

Evans [6] has given the values 97, 94, and 89 kcal./mole for the bond-dissociation energies of primary, secondary, and tertiary C–H bonds in ethane, propane, and *iso*butane, based on Stevenson's electron-impact work. It is to be expected that this variation in bond-dissociation energy would to some extent be repeated in the activation energies of reactions (2). This view is substantiated by direct determination of the activation energies of reaction (2) for ethane and *iso*butane, by Van Artsdalen and his co-workers,[7] the respective values being 13·3 and 11·4 kcal./mole.

Some General Observations on the Pyrolysis of Tertiary Organic Bromides.—All the tertiary bromides so far studied decompose either entirely or predominantly by unimolecular elimination of hydrogen bromide. The pre-exponential factors, activation energies, and rates relative to *tert.*-butyl bromide at 250° are shown in Table 6. The activation energy decreases in the series as the C–H bond changes from primary to secondary to tertiary. Though the pre-exponential factor decreases in the same order, the activation energy factor is dominant over the temperature range studied, and so the rate constant slowly increases as the C–H bond strength is reduced. This slow variation in rate contrasts strongly with that observed in the series ethyl, *iso*propyl, *tert.*-butyl bromide, where the relative rates [8] at 380° are in the ratio 1 : 170 : 32,000. This bears out the assertion [8] that the environment of the C–Br bond to be broken is the major factor determining the rate of elimination of hydrogen bromide.

TABLE 6.

Compound	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	Relative rate
C_4H_9Br	10	42·2	1
$C_5H_{11}Br$	3·98	40·5	3·2
$C_6H_{13}Br$	3·47	39·0	7·5

Of interest too is the trend in the A factors for the elimination of hydrogen bromide per β-hydrogen atom. Since there are 9, 2, and 1 β-hydrogen atoms respectively for *tert.*-butyl bromide, *tert.*-amyl bromide, and 2-bromo-2 : 3-dimethylbutane, the new A factors (A') become 1·11, 1·99, and 3·47 × 10^{13} sec.$^{-1}$ respectively. Since A' increases down the series, and E decreases, the rate sequence at all temperatures for elimination per β-hydrogen atom is *tert.*-butyl bromide > *tert.*-amyl bromide > 2-bromo-2 : 3-dimethylbutane, a simplicity of behaviour not apparent in A'. The assumption underlying this analysis is that in the transition state a given β-hydrogen atom is involved, which is, of course, satisfied by the four-centre transition state.

TABLE 7. *Mechanism of decomposition.*

	Unimolecular	Chain	Stimulated
tert.-Butyl bromide	+	—	—
tert.-Amyl bromide	+	—	+
2-Bromo-2 : 3-dimethylbutane	+	+ (?)	+

The behaviour of the three tertiary bromides already studied, as regards the mode of decomposition and the ability to stimulate reaction chains, is summarised in Table 7.

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[6] Evans, *Discuss. Faraday Soc.*, 1951, **10**, 1.

[7] Anderson and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 479, 1944; Hormats and Van Artsdalen, *ibid.*, 1951, **19**, 778.

[8] Green, Harden, Maccoll, and Thomas, *ibid.*, 1953, **21**, 178.

It is tempting to attribute the increasing tendency down the series towards a chain mechanism to the progressive changing of a β-hydrogen atom from primary to secondary to tertiary. Similarly, with primary bromides (ethyl, *n*-propyl, *iso*butyl) chains appear to be much more readily established with *iso*butyl than with *n*-propyl bromide (Harden, unpublished work).

Although re-addition of the products from *tert.*-butyl and *tert.*-amyl bromides goes to completion, that for 2-bromo-2 : 3-dimethylbutane is only partial; this may be explained in terms of the melting points. *iso*Butane, 2-methylbut-2-ene, and 2 : 3-dimethylbut-2-ene melt respectively at −140°, −134°, and −74°. Hydrogen bromide melts at −86° and boils at −67°. On condensing the products and re-vapourising them in the first two cases, the olefin will be melted while the hydrogen bromide is still solid, and this should enable reaction to take place before evaporation is complete. However, in the case of 2 : 3-dimethylbut-2-ene, the hydrogen bromide will have melted and will be close to its boiling point before the olefin melts, and in this way complete re-addition will be prevented.

Mention should be made of other studies [9] of the pyrolysis of *tert.*-butyl bromide, summarised in Table 8 (*E* was incorrectly given in Part VI as 42·0 kcal./mole). The agreement between the various authors' results is on the whole good. However, at the higher temperatures, the half-life of the reaction in Sergeev's study was of the order of 40 sec. It is just possible that with such a short half-life the time of heating of the reactant is sufficient to make the measured rate and thus the activation energy somewhat small; but experimental techniques would have to be considerably refined before an absolute decision could be made as to the Arrhenius parameters. Since, in the current series of papers, interest attaches to structural variations in related compounds, the values of the rate constants used for comparison with each other will be those determined in these laboratories, since these have been measured under strictly comparable conditions.

TABLE 8.

	Temp. range	$\log_{10} A$	E
Kistiakowsky and Stauffer [9]	235—290°	13·3	40,500
Harden and Maccoll [10]	230—280	14·00	42,200
Sergeev [11]	280—330	13·23	41,000

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[9] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.
[10] Part VI, ref. 1.
[11] Sergeev, *Doklady Akad. Nauk S.S.S.R.*, 1956, **106**, 299.