Studies in the Pyrolysis of Organic Bromides. Part VI. The Pyrolysis of* tert.*-Butyl Bromide.*†

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The present investigation confirms Kistiakowsky and Stauffer's observation that *tert.*-butyl bromide decomposes by a unimolecular mechanism in seasoned reaction vessels. This was achieved by observing the lack of inhibition of the decomposition in the presence of *cyclo*hexene and *cyclo*pentadiene. Further, allyl bromide and bromine were ineffective in stimulating a chain decomposition. Oxygen had a powerful accelerating effect. At 230—280°, the rate constant was expressible as $k_1 = 1{\cdot}0 \times 10^{14}$ exp $(-42{,}000/\boldsymbol{R}T)$ (sec.$^{-1}$), the values being independent of pressure in the range 40—400 mm.

THE thermal decomposition of *tert.*-butyl bromide into *iso*butene and hydrobromic acid has been investigated by Kistiakowsky and Stauffer (*J. Amer. Chem. Soc.*, 1937, **59**, 165) in the temperature range 235·7—291·6°. They concluded that the reaction was homogeneous and of the first order, with a velocity constant $k_1 = 10^{13{\cdot}3}$ exp $(-40{,}500/\boldsymbol{R}T)$ (sec.$^{-1}$), and that the mechanism involved was a unimolecular loss of hydrogen bromide. It seemed desirable, in connection with the present investigations, first, to study the reaction under conditions similar to those obtaining for the other bromides and, secondly, to ascertain whether the reaction could be inhibited.

EXPERIMENTAL

tert.-Butyl bromide was prepared by the hydrogen bromide–sulphuric acid method suggested by Bryce-Smith and Howlett (*J.*, 1951, 1141). Its b. p. was 73·1°/767 mm. (Timmermans, " Physical Constants of Pure Organic Compounds," Elsevier, 1950, gives b. p. 73·25°/760 mm.), and n_D^{25} was 1·4250 (Bryce-Smith and Howlett, *loc. cit.*, give n_D^{25} 1·4249). The pure bromide was stored over silver wire in the dark.

The experimental technique was essentially as described in Part I (*loc. cit.*). The bromide was admitted to the reaction vessel from a vapour reservoir. No direct investigation of the stoicheiometry of the reaction was possible, since the products recombined during the condensation. By analogy with the other bromides studied, the reaction is almost certainly :

$$C_4H_9Br \longrightarrow C_4H_8 + HBr$$

the olefin being *iso*butene. This overall reaction received confirmation from three sources. First, the final pressure (p_f) approached a value of twice the initial (p_0) (see Table 1) : it is

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* Parts I—III ; *J.*, 1955, 965, 973, 979. Parts IV and V, preceding papers.

† The Arrhenius parameters reported in this paper have previously been referred to (*J. Chem. Phys.*, 1953, **21**, 178).

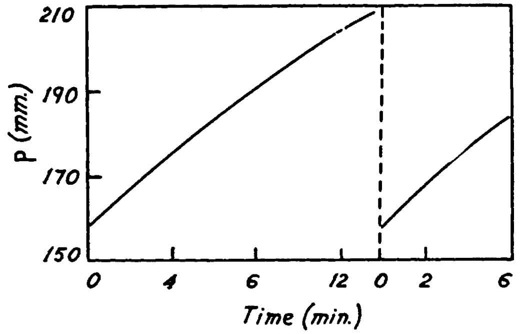
TABLE 1. *Stoicheiometry.*

Temp.	p_0 (mm.)	p_f (mm.)	p_f/p_0	Temp.	p_0 (mm.)	p_f (mm.)	p_f/p_0	Temp.	p_0 (mm.)	p_f (mm.)	p_f/p_0
277·9°	144	268	1·86	276·6°	218	403	1·85	268·6°	149	284	1·91
277·5	236	431	1·83	268·8	220	400	1·82	252·7	200	366	1·83
277·5	218	406	1·86	268·8	213	391	1·84	238·6	268	492	1·84
277·5	224	418	1·87								

somewhat less than two because (*a*), as shown by Kistiakowsky and Stauffer (*loc. cit.*), an equilibrium was set up between *tert.*-butyl bromide, *iso*butene, and hydrogen bromide, and (*b*), by virtue of the dead space inherent in the vessel used, the final pressure is not expected to reach the value $2p_0$ (Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053). Secondly, no non-condensable gases were produced. Thirdly, when the products were condensed out and then readmitted to the reaction vessel, not only were the original initial pressures reproduced, but also the rate of decomposition : this behaviour is illustrated in Table 2, where p_0 and k_1 refer to the initial runs and p_0' and k_1' to the runs after condensation (at p_f) and readmission. The behaviour is so striking that a pressure–time curve is reproduced in the Figure. Of the three butenes that could be produced, only *iso*butene would give *tert.*-butyl bromide on recombination. As the kinetic studies show that *tert.*-butyl bromide is in fact produced, it follows that the olefin formed must have been *iso*butene.

TABLE 2.

Temp.	p_0 (mm.)	10^4k_1 (sec.$^{-1}$)	p_f (mm.)	p_0' (mm.)	$10^4k_1'$ (sec.$^{-1}$)
276·0°	114	13·9	167·5	118	13·7
259·4	158	4·78	208	158	4·99



Pressure–time curve, showing the essential reversibility of the reaction. The reaction was stopped and then restarted, at the broken line.

Some preliminary runs were carried out in a clean-walled Pyrex vessel at 258·5° and 272·9°. In no case was a change of pressure with time observed. A weighed sample of *tert.*-butyl bromide was then admitted to the system, and, after 90 sec. the pressure was 440 mm., whereas the calculated initial pressure was about 180 mm. This shows that the reaction is very fast in clean Pyrex vessels. The remainder of the runs were done in a Pyrex reaction vessel which had been seasoned by the pyrolysis products of allyl bromide.

In order to check the first-order character of the decomposition, a series of runs were done at 276·6°, with initial pressures varying from 48 to 446 mm. The rate constants derived are shown in Table 3. The first-order rate constants varied by a maximum of ±6% from the mean value, but no systematic trend was observable. In view of the fact that Kistiakowsky and Stauffer (*loc. cit.*) had reported the homogeneous nature of the decomposition, it was not thought necessary to measure the rates in packed vessels.

TABLE 3.

p_0 (mm.)	$10^3k_{0·5}$ (mm.$^{\frac{1}{2}}$ sec.$^{-1}$)	10^4k_1 (sec.$^{-1}$)	$10^5k_{1·5}$ (mm.$^{-\frac{1}{2}}$ sec.$^{-1}$)	p_0 (mm.)	$10^3k_{0·5}$ (mm.$^{\frac{1}{2}}$ sec.$^{-1}$)	10^4k_1 (sec.$^{-1}$)	$10^5k_{1·5}$ (mm.$^{-\frac{1}{2}}$ sec.$^{-1}$)
446	32·00	15·91	7·03	217·5	22·00	16·63	10·20
379	33·33	16·67	8·93	150·5	21·33	17·62	14·47
294·5	28·67	16·85	9·93	123·6	17·33	16·89	14·50
247	26·67	16·97	11·20	91·0	14·13	17·06	16·00
218	22·67	15·78	10·73	48·3	11·20	17·62	23·33

The variation of the rate constants with temperature was determined in the range 231—284°: see Table 4. From the plot of log k against the reciprocal of the absolute temperature, the rate was found to be expressible as $k = 10^{14\cdot0} \exp(-42{,}000/\boldsymbol{R}T)$ (sec.$^{-1}$).

TABLE 4.

No. of runs	Temp.	10^4k_1 (sec.$^{-1}$)	No. of runs	Temp.	10^4k_1 (sec.$^{-1}$)	No. of runs	Temp.	10^4k_1 (sec.$^{-1}$)
5	282·4°	24·25	3	266·1°	7·68	3	243·3°	1·31
6	280·7	21·31	10	261·5	5·51	4	240·0	1·09
10	276·6	16·80	6	255·6	3·41	3	235·5	0·709
7	272·9	12·41	4	255·1	3·33	4	231·2	0·467
5	272·2	12·27	3	247·9	1·94			

The main purpose of the work described here was to examine the reaction in the presence of inhibitors, to verify whether or not the reaction proceeds by a unimolecular elimination. Two inhibitors were used, *cyclo*hexene and *cyclo*pentadiene, both having been found by P. J. Thomas (personal communication) to be highly efficient in inhibiting the chain mechanism in the decomposition of *n*-propyl bromide (cf. Part II). Only a single temperature was used in each case. The results, shown in Table 5, p_i representing the pressure of inhibitor, give no evidence of inhibition, within the limits of experimental error.

TABLE 5.

Inhibitor: cyclo*hexene*. *Temp.*, 273·2. $k_{\text{calc.}} = 12\cdot47 \times 10^{-4}$ (sec.$^{-1}$).

p_0 (mm.)	302	259	288	305	249	311	303	316
p_i (mm.)	0	0	7	19·5	32	34	40·5	41·5
10^4k_1 (sec.$^{-1}$)	12·48	12·67	12·57	12·33	12·95	12·44	11·72	12·79

Inhibitor: cyclo*pentadiene*. *Temp.*, 265·7°. $k_{\text{calc.}} = 7\cdot28 \times 10^{-4}$ (sec.$^{-1}$).

p_0 (mm.)	257	207	140	218	222	221	246
p_i (mm.)	0	0	10·5	54·5	87·5	98	121
10^4k_1 (sec.$^{-1}$)	6·99	7·49	6·91	6·72	6·97	7·22	6·95

Since there is no chain component in the normal decomposition in seasoned vessels, the addition of chain-stimulating substances was tried. Molecular bromine provides an obvious source of bromine atoms, and Daniels and Veltman (*J. Chem. Phys.*, 1939, **7**, 756) have shown it to catalyse powerfully the decomposition of ethyl bromide. Thomas (personal communication) has shown that decomposing allyl bromide will also provide a concentration of bromine atoms (cf. Part I, *loc. cit.*) capable of stimulating a chain mechanism in bromide pyrolyses. Finally methyl iodide would be a source of both methyl radicals and iodine atoms, which might conceivably initiate reaction chains. The results of pyrolysis carried out in the presence of these substances, shown in Table 6 (the pressure of added stimulant is represented by p_s), provide no evidence of *tert.*-butyl bromide's supporting a radical-chain mechanism.

TABLE 6.

Stimulant: *molecular bromine.* *Temp.*, 264·4°. $k_{\text{calc.}} = 6\cdot70 \times 10^{-4}$ (sec.$^{-1}$).

p_0 (mm.)	p_s (mm.)	10^4k_1 (sec.$^{-1}$)
304	0	6·83
206	0	6·81
252	19	6·93
220	44	6·49
367	46·5	6·72

Stimulant: *allyl bromide.* *Temp.*, 265·3°. $k_{\text{calc.}} = 7\cdot13 \times 10^{-4}$ (sec.$^{-1}$).

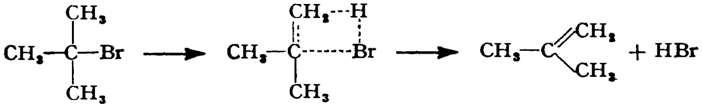
p_0 (mm.)	p_s (mm.)	10^4k_1 (sec.$^{-1}$)
352	0	6·82
306	52	6·77
276	53	6·80
167	68	6·55

Stimulant: *methyl iodide.* *Temp.*, 266·5°. $k_{\text{calc.}} = 7\cdot76 \times 10^{-4}$ (sec.$^{-1}$).

p_0 (mm.)	p_s (mm.)	10^4k_1 (sec.$^{-1}$)
281	0	7·25
227	0	7·87
243	36	7·81
275	45·5	7·79
147	56	7·60
258	92·5	7·10

DISCUSSION

Pyrolysis of *tert.*-butyl bromide in the gaseous phase in seasoned reaction vessels has been shown to be a first-order, homogeneous reaction, as concluded by Kistiakowsky and Stauffer (*loc. cit.*). Further, the inability of established olefinic inhibitors to alter the rate may be taken as proof of the unimolecular nature of the reaction. There is little doubt that the reaction investigated takes place by the four-centre transition-state mechanism:



This type of mechanism has also been reported (Parts III—V) to occur with those compounds studied containing C–Br links in secondary groups, namely, *sec.*-propyl, *sec.*-butyl, and *cyclo*hexyl bromide. This sharply distinguishes the secondary and the tertiary from the primary compounds. It seems highly probable that ethyl bromide decomposes at least partially by a chain mechanism (Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 756). Again it was shown in Part II that *n*-propyl bromide decomposes by a chain process. It is of interest that the relative rates of pyrolysis of *sec.*-propyl and *tert.*-butyl bromide at 360° are approximately 1 : 170, an extrapolated value being used for *tert.*-butyl bromide.

It should be noted that in the temperature range investigated, all the rates reported here are somewhat lower than those reported by Kistiakowsky and Stauffer. It is difficult to see any mechanism for retarding a strictly unimolecular decomposition, and so it is believed that the present parameters are the more reliable.

The other factor that emerges from this work is the inability to induce chains, even in the presence of a relatively high pressure of bromine, although all radicals produced by bromine atom attack are P-radicals in the nomenclature of Part III. This observation bears out the view put forward there that the production of chains depends at least in part upon ease of bromine atom attack on a C–H bond in a secondary group. Thus in *n*-propyl bromide, P-radicals are produced by an attack on a methylene group,* while in *sec.*-propyl bromide and *tert.*-butyl bromide they are only produced by an attack on a methyl group.

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