Studies in the Pyrolysis of Organic Bromides. Part IV. The Pyrolysis of* sec.*-Butyl Bromide.*

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sec.-Butyl bromide has been shown to decompose to butene and hydrobromic acid in the temperature range 300—350° homogeneously and according to a first-order law. The rate constant is expressible as $k_1 = 4{\cdot}27 \times 10^{12} \exp(-43{,}800/\boldsymbol{R}T)$ (sec.$^{-1}$). Added propene and *cyclo*hexene do not radically alter the rate and it is concluded that the predominant process is the unimolecular elimination of hydrogen bromide.

IN Parts I—III,* three distinct mechanisms have been observed for the pyrolyses of organic bromides in the gaseous phase : allyl bromide decomposes by a radical non-chain process, *n*-propyl bromide by a radical-chain mechanism, and *iso*propyl bromide by direct unimolecular elimination of hydrogen bromide. The essential steps in the chain mechanism are :

$$\mathrm{RBr} \longrightarrow \mathrm{R} + \mathrm{Br} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\mathrm{Br} + \mathrm{RBr} \longrightarrow \mathrm{R'Br} + \mathrm{HBr} \quad \ldots\ldots\ldots \quad (2)$$

$$\mathrm{R'Br} \longrightarrow \mathrm{M} + \mathrm{Br} \quad \ldots\ldots\ldots\ldots \quad (3)$$

together with some chain-ending step (M represents an olefin). The case of allyl bromide is distinctive in that the allyl radical $CH_2{-}\overset{\frown}{CH_2}{-}CH_2$ is strongly stabilised by resonance, as is also true of the bromoallyl radical $CH_2{-}\overset{\frown}{CH_2}{-}CHBr$. The non-chain character of the pyrolysis can in the main be ascribed (1) to the weakness of the C–H bond in the CH_2Br group, so that attack by a bromine atom is directed to this group, and (ii) to the lack of facility of the chain-propagating step (3). The behaviour of the propyl bromides has been explained in terms of propagating (P) radicals and stopping (S) radicals, *viz.* :

$CH_3{\cdot}\dot{C}H{\cdot}CH_2Br$ (P)	$CH_3{\cdot}CHBr{\cdot}\dot{C}H_2$ (P)
$CH_3{\cdot}CH_2{\cdot}\dot{C}HBr$, $\dot{C}H_2{\cdot}CH_2{\cdot}CH_2Br$ (S)	$(CH_3)_2\dot{C}Br$ (S)

It has been shown in Part III that the atom attack on *n*-propyl bromide leads in the main to P radicals, whereas in *iso*propyl bromide it leads to S radicals. Further the P radicals

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* Parts I—III, *J.*, 1955, 965, 973, 979.

from *n*-propyl bromide decompose very much more rapidly than those from *iso*propyl bromide. The observed case of chain propagation in *n*-propyl bromide and its absence in *iso*propyl bromide are thus explained.

The pyrolysis of *sec.*-butyl bromide poses two questions : First, what effect, on the rate of unimolecular elimination of hydrogen bromide, has the replacement of a C–H bond in which the C atom is primary by one in which it is secondary? Secondly, will the chain mechanism be favoured by the fact that the P radicals can be produced by an attack on the C–H bond of a secondary group ? That the unimolecular mechanism might be preferred is indicated in the literature : ethyl bromide (Lessig, *J. Phys. Chem.*, 1932, **36**, 225 ; Vernon and Daniels, *J. Amer. Chem. Soc.*, 1933, **55**, 922 ; Fugassi and Daniels, *ibid.*, 1938, **60**, 771 ; Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 756 ; Roof and Daniels, *J. Amer. Chem. Soc.*, 1940, **62**, 2912 ; Roof, *ibid.*, 1944, **66**, 358) and *n*-propyl bromide (Part II) decompose by a chain mechanism, at least in part in the former case, whereas *sec.*-propyl bromide (Part III) and *tert.*-butyl bromide * (Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165) decompose by unimolecular elimination of hydrogen bromide. This suggests that the nature of the C–Br bond is the most cogent factor in determining the mode of decomposition.

EXPERIMENTAL

Two commerical samples of *sec.*-butyl bromide were fractionated through a metre column, the middle fractions of constant physical properties being retained. Secondly, the bromide was prepared by treatment of fractionated *sec.*-butyl alcohol with constant-boiling hydrobromic acid. All samples showed the same kinetic behaviour. The b. p. was 91·4°/760 mm. (cf. Timmermans, " Physical Constants of Pure Organic Compounds," Elsevier, Netherlands, 1950, reports 91·2°, 91·24°, 91·3°), n_D^{25} 1·4342 (cf. Heston *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 2072, who report 1·4342).

By analogy with the pyrolysis of other saturated bromides it may be concluded that the overall reaction is :

$$C_4H_9Br \longrightarrow C_4H_8 + HBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As in the previous studies, the kinetics of the reaction were measured by studying both the rate of pressure increase and the rate of production of hydrogen bromide. Table 1 illustrates the agreement between the two methods. After a run, the products were completely condensable in liquid air, so it may be concluded that equation (4) represents the course of the decomposition.

TABLE 1.

Method	Decomposition (%)									
Pressure	30·6	43·2	46·1	57·2	59·0	66·0	70·0	82·6	83·2	89·3
Anal.	30·7	44·6	46·0	58·5	59·3	65·8	71·0	83·5	81·9	89·2

The reaction followed a first-order law up to about 50% decomposition (see Fig. 1). The subsequent decrease in rate is best interpreted, as for *iso*propyl bromide, in terms of an equilibrium between (4) and the reverse reaction. That the first-order law is obeyed over a wider range implies that the equilibrium lies further towards the right. The homogeneity of the reaction was tested in the usual manner by packing the reaction vessel with thin-walled glass tubing, so as to increase the surface : volume ratio by a factor of five. The results obtained at two temperatures are shown in Table 2.

TABLE 2.

	At 311°.				*At* 333°						
p_0 (mm.)	342	325	280	267	350	335	276	254	227	206	187
$10^4 k_1$ (sec.$^{-1}$)	1·66	1·68	1·70	1·72	6·95	7·02	6·78	7·02	7·12	7·02	6·95

The mean values $1·69 \times 10^{-4}$ and $7·00 \times 10^{-4}$ sec.$^{-1}$, compared with the values for the unpacked vessel, $1·70 \times 10^{-4}$ and $6·61 \times 10^{-4}$ sec.$^{-1}$ (interpolated from the Arrhenius equation), show that the five-fold increase in the surface : volume ratio had little effect on the rate.

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* The pyrolysis of *tert.*-butyl bromide has been re-investigated by G. D. Harden (Part VI), who has unambiguously demonstrated unimolecular elimination.

The variation of the reaction rate with temperature, in the range 300—350°, is set out in Table 3. The experimental results were fitted to the equation

$$k_1 = 4{\cdot}27 \times 10^{12} \exp(-43{,}800/\boldsymbol{R}T)$$

the agreement between the observed and calculated values being excellent. The Arrhenius plot is shown in Fig. 2.

In order to test the pressure dependence of the rate constants over a wide pressure range, a number of runs were carried out at 333° (see Table 4) : there was no effect on the rate. The value at high pressures is slightly greater than that ($6{\cdot}70 \times 10^{-4}$ sec.$^{-1}$) obtained from the Arrhenius plot, perhaps because these experiments were performed in a rebuilt apparatus employing a vapour reservoir.

FIG. 1. *The first-order plot, showing a departure from linearity after about* 50% *reaction.*

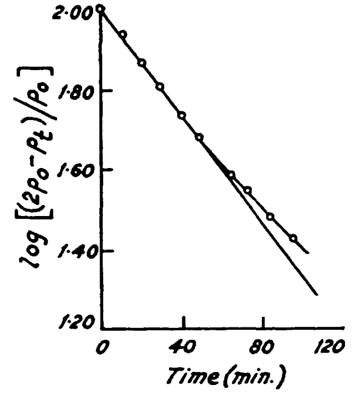

FIG. 2. *The Arrhenius plot.*

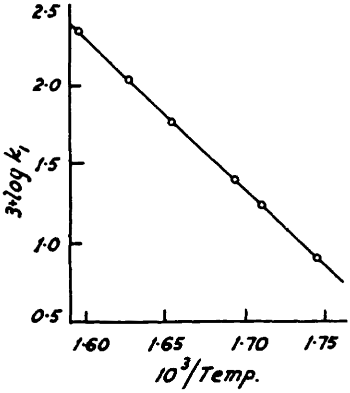

TABLE 3.

Temp.	299·5°	311·5°	317°	331·5°	341·5°	353°
No. of runs	7	7	7	6	3	4
10^4k_1 (sec.$^{-1}$)	0·717	1·71	2·49	5·98	10·8	21·9

TABLE 4. *Effect of pressure, at* 333°.

p_0 (mm.)	343	327	308	230	215	164	118	114	84
10^4k_1 (sec.$^{-1}$)	7·02	6·78	6·78	7·16	7·06	6·78	7·58	7·46	7·01
p_0 (mm.)	67	66·5	52	48·5	43	36·5	31	25	25
10^4k_1 (sec.$^{-1}$)	6·80	7·04	7·31	7·60	7·22	7·00	7·50	7·16	7·21

In order to test for the presence of bromine-atom chains, the decomposition was carried out in the presence of propene and *cyclo*hexene. The latter should be a particularly efficient inhibitor because of the C–H bond, in which the C is primary and adjacent to the double bond. Attack by a bromine atom would be facilitated both by this and by the resonance stabilisation of the *cyclo*hexenyl radical (cf. allyl). That *cyclo*hexene is in fact a powerful inhibitor has been shown in the case of *n*-propyl bromide. (The relative efficiencies of different inhibitors are under investigation and will be reported later.)

TABLE 5. *Effect of added propene* (p_i) ; *at* 325°.

T	p_0 (mm.)	p_i (mm.)	10^4k_1 (sec.$^{-1}$)	10^4k_1 (sec.$^{-1}$; calc.)	T	p_0 (mm.)	p_i (mm.)	10^4k_1 (sec.$^{-1}$)	10^4k_1 (sec.$^{-1}$; calc.)
322°	239	97	3·44	3·35	322°	215	190	3·14	3·35
323	231	144	3·62	3·55	324	295	291	3·51	3·80
324	216	146	3·54	3·80					

The results of the runs in the presence of added propene (pressure p_i) are shown in Table 5. There is a slight tendency for the rate to be less in the presence of added propene, but the experimental scatter precludes quantitative conclusions. It is obvious, however, that no marked inhibition occurs and hence it may be concluded that the reaction is predominantly non-chain in character. This conclusion is borne out by the experiments in the presence of added *cyclo*hexene (see Table 6), the mean values of k in its absence and presence being $4{\cdot}05 \times 10^{-4}$ and $3{\cdot}75 \times 10^{-4}$ sec.$^{-1}$, respectively.

TABLE 6. *Effect of added* cyclo*hexene, at* 325°.

p_0 (mm.)	209	280	418	455	328	299	260	240	310
p_i (mm.)	0	0	0	0	110	120	130	140	200
$10^4 k_1$ (sec.$^{-1}$)	3·97	4·10	4·16	3·97	3·73	3·80	3·67	3·75	3·82

DISCUSSION

The experimental results may be summarised as follows: (*a*) The pyrolysis of *sec.*-butyl bromide proceeds according to equation (4) in the temperature range 300—350°. (*b*) The reaction follows a first-order law, at least in the early stages where complications due to the reverse reaction may be neglected (for rate constants see above). (*c*) The first-order constants show no significant pressure variation over the range 25—350 mm. initial pressure. (*d*) The rate of reaction in the initial stages is unaffected by the addition of *cyclo*hexene or propene. (*e*) Increasing the inhibitor pressures cause the rate to depart from the first-order law at an earlier stage in the reaction.

The first-order rate law is consistent with a mechanism involving unimolecular elimination of hydrogen bromide, and with a chain mechanism involving bromine atoms, initiated by the breaking of the C–Br bond, but the latter is excluded by factor (*d*) above.

The effect (*e*), for *iso*propyl bromide, was attributed to the equilibrium $C_3H_7Br \rightleftharpoons C_3H_6 + HBr$. This phenomenon will in the present work be complicated by competition between the reactions, $C_4H_8 + HBr \rightleftharpoons C_4H_9Br$, and $C_3H_6 + HBr \rightleftharpoons C_3H_7Br$, or $C_6H_{10} + HBr \rightleftharpoons C_6H_{11}Br$. It is also found that the effect is not so marked as with *iso*propyl bromide.

The structure of the butene produced has not been studied. In the case of the chain mechanism, it appears likely that attack would be upon the secondary group, leading to but-2-ene. However, since little is as yet known about the effect of structure upon parameters of the Arrhenius equation for the unimolecular elimination, no definite conclusion can be drawn. It is perhaps suggestive that the activation energy is less than for *iso*propyl bromide, which may be due to energy differences between elimination involving hydrogen from secondary and primary groups.

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