36. *Studies in the Pyrolysis of Organic Bromides. Part XIV.* The Unimolecular Decomposition of* n-*Pentyl and* n-*Hexyl Bromides.*

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The pyrolyses of n-pentyl and n-hexyl bromides in the presence of cyclohexene in " seasoned " reaction vessels have been investigated over the temperature range 370—420°. The reaction is in each case a first-order, homogeneous decomposition into an olefin and hydrogen bromide. The rate constants are given by:

n-Pentyl bromide: $k_1 = 1.23 \times 10^{13} \exp(-50,500/RT)$ sec.$^{-1}$

n-Hexyl bromide: $k_1 = 1.35 \times 10^{13} \exp(-50,500/RT)$ sec.$^{-1}$

No pressure-dependence of k_1 was detected over a wide range of initial pressures, and the processes have been shown to be unimolecular eliminations.

WHEREAS organic bromides containing secondary and tertiary C–Br bonds predominantly decompose by a mechanism involving unimolecular elimination of hydrogen bromide (Parts III—IX, XI *), those containing primary C–Br bonds decompose by a simultaneous unimolecular and chain mechanism (Parts II, X, XII, XIII). The latter mode of decomposition can be suppressed by the addition of an olefinic inhibitor such as propene or, better, cyclohexene (Part X), with the consequent isolation of the former. For the primary bromides $CH_3 \cdot [CH_2]_n \cdot CH_2Br$ it seems reasonable to expect the rate of decomposition to approach a limit as *n* increases. The object of this paper is to test this.

EXPERIMENTAL

Both bromides were prepared by refluxing a carefully fractionated sample of the corresponding alcohol with a mixture of hydrobromic acid and sulphuric acid, followed by distillation The lower bromide layer was washed with aqueous hydrobromic acid, dilute sodium carbonate, and then water, dried (CaCl₂), and fractionated. It was found necessary rigorously to adhere to this procedure; in the case of n-hexyl bromide, a commercial sample even after repeated fractionation showed the phenomenon of " fast starts." The physical constants of the samples used were: n-pentyl bromide, b. p. 51·0°/51 mm.[1] (value interpolated from values in the literature of 128·8°/760 mm.[2] and 34·7°/22 mm.[3] is 52·1°/51 mm.), n_D^{25} 1·4420 (lit.,[2] 1·4427); n-hexyl bromide, b. p. 81·5°/79 mm., 76·7°/60 mm. (values interpolated from values in the literature of 155·5°/743·8 mm.,[3] 88·0°/70 mm.,[3] 55·3°/24 mm.[2] are 84·7°/79 mm., 76·7°/60 mm.), n_D^{25} 1·4451, 1·4455 (lit., 1·4452,[3] 1·4461 [2]).

The apparatus and technique were essentially as in Part I, the reactant being distilled into the reaction vessel from a small phial introduced into the side arm. The pyrolyses were performed in vessels seasoned by the decomposition products of allyl bromide. Chain decomposition was inhibited by cyclohexene, which was admitted from a vapour reservoir. By analogy with the decomposition of the other bromides, the pyrolysis would be expected to follow the reaction

$$C_nH_{2n+1}Br \longrightarrow C_nH_{2n} + HBr \qquad \qquad \text{. . . . . (1)}$$
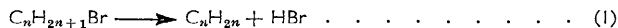
This was checked (i) by measurements of the ratio of final to initial pressure, and (ii) by comparison of the percentage decomposition calculated from the pressure measurements on the basis of eqn. (1) with those directly determined from the HBr produced (Table 1). For both the inhibited and uninhibited decompositions of n-pentyl bromide, the ratios of final to initial pressure were all *ca.* 1·97 for initial pressures of 125 to 289 mm. and temperatures from 390° to 426°.

* Maccoll *et al.*, *J.*, 1955, 965 (Part I), 973 (Part II), 979 (Part III), 2445 (Part IV), 2449 (Part V), 2454 (Part VI); 1957, 5020 (Part VII), 5024 (Part VIII), 5028 (Part IX), 5033 (Part X); 1958, 3016 (Part XI); 1959, 1192 (Part XII), 1197 (Part XIII).

[1] Krishner, Crowe, and Smythe, *J. Amer. Chem. Soc.*, 1950, **72**, 1091.
[2] Heston, Hennely, and Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 2071.
[3] Ellis and Read, *J. Amer. Chem. Soc.*, 1932, **54**, 1674.

TABLE 1. *Stoicheiometry of the reaction.*

n-Pentyl bromide

Temp.	399°	421°	406°	394°	417°
Decomp. (%, press.)	10·9	28·2	48·6	56·2	67·3
Decomp. (%, anal.)	11·1	27·8	48·3	56·4	66·8

n-Hexyl bromide

Temp.	372°	380°	386°	384°	408°	405°	410°	410°
Decomp. (%, press.)	17·6	25·3	29·7	38·5	53·4	57·6	78·3	86·3
Decomp. (%, anal.)	17·4	25·7	29·2	38·9	53·9	57·4	78·0	85·8

Analytical results for prolonged (overnight) uninhibited decompositions of n-pentyl bromide were appreciably lower than those from pressure measurements, *e.g.*, 97·3% (press.), 95·9% (anal.); also, whereas the products of reaction were completely condensable in liquid air for runs taken to 50% decomposition, this was not so in the region of 95% decomposition. These facts, coupled with the high $p_{\text{final}}/p_{\text{initial}}$ ratios, suggest a secondary decomposition of the pentene produced. It may be inferred from Molera and Stubbs's [4] results that the half-life of pent-1-ene at 400° is *ca.* 30 hr.

Homogeneity of the inhibited reactions was proved by means of a vessel packed with Pyrex tubing so that the surface : volume ratio was approximately trebled (Table 2).

TABLE 2. *Homogeneity of the reaction.*

	n-Pentyl bromide				n-Hexyl bromide				
Temp.	371·5°	379·5°	392°	405·5°	389·5°	403°	403°	420°	421°
$10^4 k_1$ (sec.$^{-1}$) (unpacked)	0·953	2·91	3·24	6·92	3·02	6·49	6·49	16·2	17·3
$10^4 k_1$ (sec.$^{-1}$) (packed)	0·981	2·89	3·29	7·13	3·02	6·38	6·46	16·2	17·2

The values for the rates in unpacked vessel were obtained from the relevant Arrhenius equation (Table 5). The reactions studied are clearly homogeneous.

In order to show that the reaction was really the maximally inhibited reaction, runs with various inhibitor (cyclohexene) pressures (p_i) were carried out (Table 3). No significant

TABLE 3. *Dependence of rate coefficients on inhibitor pressure.*

	n-Pentyl bromide at 405°					n-Hexyl bromide at 400°				
p_i (mm.)	89	105	111	137	215	76	97	107	115	172
p_o (mm.)	180	167	173	243	225	131	173	128	151	238
$10^4 k_1$ (sec.$^{-1}$)	6·68	7·16	6·76	7·36	6·28	5·16	5·61	5·66	5·06	5·32

variation in the rate was observed over an approximately 2·5-fold range of inhibitor pressure. The reactions are of the first order (Table 4). Over a fifteen-fold variation of initial pressure

TABLE 4. *First-order nature of the decomposition.*

n-Pentyl bromide at 405°.

p_o (mm.)	337	307	287	259	243	225	180	173
$10^4 k_1$ (sec.$^{-1}$)	7·21	7·25	6·88	6·69	7·36	6·28	6·68	6·76
p_o (mm.)	167	143	119	97	53·5	47	29	22
$10^4 k_1$ (sec.$^{-1}$)	7·16	7·01	7·00	6·72	6·24	6·84	6·80	6·77

n-Hexyl bromide at 410°.

p_o (mm.)	268	223	173	124	103	75	67	33
$10^4 k_1$ (sec.$^{-1}$)	9·93	9·54	9·25	9·27	9·13	9·34	9·33	9·55

TABLE 5. *Temperature-dependence of the rate constants.*

n-Pentyl bromide.

Temp. (No. of runs)	425° (8)	410° (7)	405° (16)	400° (7)	390° (5)	372° (5)
$10^4 k_1$ (sec.$^{-1}$)	19·8	8·85	6·86	5·23	2·86	1·00

n-Hexyl bromide.

Temp. (No. of runs)	420° (3)	410° (8)	400° (7)	390° (3)	380° (3)	370° (3)
$10^4 k_1$ (sec.$^{-1}$)	16·22	9·41	5·60	3·08	1·78	0·933

for n-pentyl bromide and an eight-fold variation for n-hexyl bromide, there is no significant trend in the rate constants. The mean velocity constants obtained in the investigation of the temperature-dependence of the rate constants are shown in Table 5.

[4] Molera and Stubbs, *J.*, 1952, 381.

The Arrhenius plots yielded the equations

n-Pentyl bromide: $k_1 = 1.23 \times 10^{13} \exp(-50,500/RT) \text{ sec.}^{-1}$

n-Hexyl bromide: $k_1 = 1.35 \times 10^{13} \exp(-50,500/RT) \text{ sec.}^{-1}$

Within the limits of experimental error, the activation energies are the same for the two compounds. The slight increase in rate in going from n-pentyl to n-hexyl bromide is probably due to the small increase in the pre-exponential factor.

DISCUSSION

In the presence of cyclohexene, n-pentyl and n-hexyl bromides decompose homogeneously in seasoned reaction vessels. The rate of decomposition is independent of the pressure of inhibitor within wide limits. In view of the evidence presented in Part X it was not considered necessary to show that the maximally inhibited rate was independent of the nature of the inhibitor. Further, the rate of pressure increase obeys the first-order rate law up to at least 50% decomposition. Since a chain mechanism has been eliminated by working at maximal inhibition, the likely mechanisms remaining are a radical non-chain process (cf. ethyl bromide [5]) or a unimolecular elimination. The former process can be ruled out by the observed activation energy, which for such a scheme should be of the order of the primary C–Br bond dissociation energy (*ca.* 67 kcal./mole). It may thus be concluded that the mechanism is a unimolecular elimination. Further evidence for this conclusion is presented below.

General Conclusions concerning the Unimolecular Decomposition of Primary Bromides.—The results so far obtained for the unimolecular decomposition of primary organic bromides are in Table 6, the references being to earlier Parts. Perhaps the most interesting con-

TABLE 6. *Arrhenius parameters for primary bromide pyrolyses.*

Bromide	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	Part
Ethyl	2·63	53·9	XI
n-Propyl	0·79	50·7	X
n-Butyl	1·51	50·9	X
n-Pentyl	1·23	50·5	XIV
n-Hexyl	1·35	50·5	XIV
Isobutyl	1·12	50·4	XII

clusion to be drawn from this series is the constancy of the activation energy, apart from that for ethyl bromide. It is of interest to compare the rates, relative to those of ethyl bromide and chloride taken as unity, at 380° (Table 7). Although there is a steady increase in rate on going along the series, a limiting rate is rapidly approached. After n-butyl bromide, the reaction centre is affected little by increase in length of the alkyl

TABLE 7. *Relative rates of dehydrohalogenation.*

R	Ethyl	n-Propyl	n-Butyl	n-Pentyl	n-Hexyl
R–Br	1	3·6	5·9	6·3	6·8
R–Cl	1 [a]	4·1 [b]	5·9 [b]		

[a] Barton and Howlett, *J.*, 1949, 165. [b] Barton, Head, and Williams, *J.*, 1951, 2039.

chain. As there is no complication in the case of the chlorides due to a concurrent chain reaction, the similarity of behaviour between the bromides and the chlorides serves as further confirmation of the unimolecular nature of the maximally inhibited bromide pyrolyses.

The relative proportions of chain and unimolecular processes in the series of primary bromides is enlightening. Although a full investigation of the uninhibited reactions has not been made, rates at 380° are obtainable (Table 8). Apart from the increase at n-propyl bromide, the chain rate decreases uniformly down the series. The increase from ethyl to n-propyl bromide may be attributed to the fact that the P radicals (cf. Part III) formed by

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

bromine atom attack on the parent bromide are obtained from primary and secondary C–H bonds respectively. This process will be easier in the case of n-propyl bromide. The decrease in chain rate from n-butyl to n-hexyl bromide may be attributed to a probability factor for attack at the right position to form a P radical. Thus for $CH_3 \cdot [CH_2]_n \cdot CH_2Br$

TABLE 8. *Comparison of the unimolecular and chain components in dehydrobromination.*

Bromide	Total rate	$10^4 k_1$ (sec.$^{-1}$) Inhibited rate	Chain rate	Chain component (%)
Ethyl	2·14	0·26	1·88	90
n-Propyl *	9·97	0·87	9·10	93
n-Butyl	2·92	1·37	1·55	53
n-Pentyl	2·92	1·59	1·33	46
n-Hexyl	2·72	1·71	1·10	37

* For this compound, k_1 was calculated at 300 mm. from the published $k_{1.5}$ (Part II).

$(n > 1)$ if it is assumed that all secondary C–H bonds are equally liable to attack, the probabilities of forming an S radical and a P radical are proportional to $2n - 2$ and 2 respectively. Hence the fraction of attacks leading to a P radical is proportional to $1/n$. This ratio for the bromides from n-butyl to n-hexyl is 0·5, 0·33, 0·25, a series which bears some resemblance to that in the fourth column of Table 8. The overall change in the total rate down the series is a combination of the decreasing chain rate and increasing unimolecular rate.