1004. *Studies in the Pyrolysis of Organic Bromides. Part VII.* The Maximally Inhibited Decomposition of* cyclo*Pentyl Bromide.*

By M. N. Kale and Allan Maccoll.

Gas-phase pyrolysis of *cyclo*pentyl bromide over the temperature range 300—360° proceeds homogeneously according to a first-order law by a mixed chain and unimolecular mechanism, the latter predominating. The temperature-dependence of the rate constants was represented by $k = 1{\cdot}29 \times 10^{12} \exp(-41{,}590/\boldsymbol{R}T)$ (sec.$^{-1}$). The reaction is also homogeneous and of the first order in the presence of added *cyclo*hexene, so under these conditions the mechanism is unimolecular. The rate constants were fitted to the equation, $k = 6{\cdot}92 \times 10^{12} \exp(-43{,}700/\boldsymbol{R}T)$ (sec.$^{-1}$). The relation of this result to those for other secondary bromides and to certain reactions in polar solvents is discussed in the light of an analogy proposed by Maccoll and Thomas.

In continuation of our investigations into the structural factors influencing the rates of pyrolysis of organic bromides, the present work describes a study of the pyrolysis of *cyclo*pentyl bromide in the absence and in the presence of *cyclo*hexene. In Part V,[1] the pyrolysis of *cyclo*hexyl bromide was shown to proceed by a homogeneous unimolecular mechanism, involving elimination of hydrogen bromide. In particular, the rate of pyrolysis was unaffected by added *cyclo*hexene. In the present case, however, a small, but significant, difference was caused by added *cyclo*hexene.

After this work was complete, Price, Shaw, and Trotman-Dickenson [2] reported results confirming ours on the thermal decomposition of *cyclo*pentyl bromide, except as regards the effect of *cyclo*hexene. This difference may be due to the low molar ratio of *cyclo*hexene used by Price *et al.* A further significant difference was the presence of short induction periods, corresponding to 2—3% of decomposition, not observed by us for this or any bromide decomposing by a unimolecular mechanism.

Experimental

*cyclo*Pentyl bromide was prepared from *cyclo*pentanol and hydrogen bromide. On distillation through a 1-m. column packed with glass helices, a fraction having b. p. 136·0°/765 mm., n_D^{25} 1·4867, was collected (lit., 135—136°/760 mm.,[3] n_D^{25} 1·4866 [4]). Decomposition of the bromide was followed (cf. earlier papers) by measuring the rate of pressure increase in an all-glass apparatus. The stoicheiometry of the reaction was verified by comparing the amount decomposition calculated from the pressure increase with that obtained by direct titration of the hydrogen bromide produced. The irreproducibility found by Price *et al.* was not apparent in the present work.

Justification for the overall reaction

$$C_5H_9Br = C_5H_8 + HBr \qquad (1)$$

in the absence and presence of *cyclo*hexene is shown in Table 1, which presents a representative selection of results obtained. Runs marked h were carried out in the presence of *cyclo*hexene.

Table 1. *Decomposition at* 318·2°.

Decompn. (%) (press.)	12·4	22·5h	29·0	47·7h	66·1	72·3h	85·7
Decompn. (%) (anal.)	12·2	22·0h	28·6	49·0h	64·9	73·5h	84·5

Rate constants have been calculated on the basis of eqn. (1). The homogeneity of the reaction was tested by increasing the surface : volume ratio of the reaction vessel by a factor of five, by

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* Part VI, *J.*, 1955, 2454.

[1] Green and Maccoll, *J.*, 1955, 2449.

[2] Price, Shaw, and Trotman-Dickenson, *J.*, 1956, 3856.

[3] Moller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1080.

[4] Rogers and Roberts, *ibid.*, 1946, **68**, 843.

TABLE 2. *Effect of surface : volume ratio* (10^4k_1 in sec.$^{-1}$).

	No *cyclo*hexene		*cyclo*Hexene added	
Temp.	Packed (obs.)	Unpacked (calc.)	Packed (obs.)	Unpacked (calc.)
341·8°	20·3	20·5	19·2	19·5
324·8	7·89	7·85	7·06	7·08
306·8	2·72	2·64	2·32	2·27

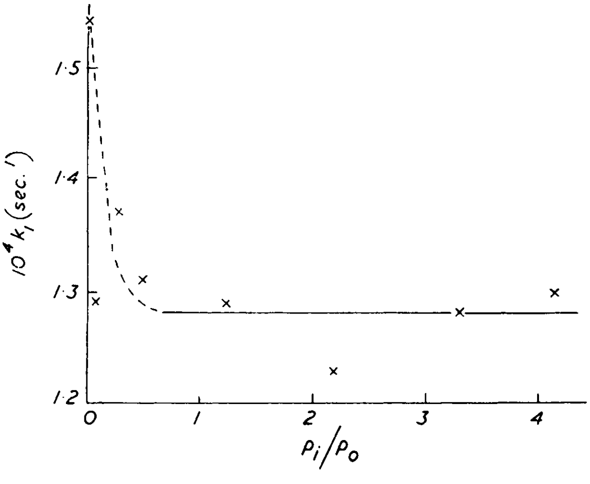
TABLE 3. *Effect of variation of initial pressure.*

Uninhibited reaction at 327·8°.							
p_0 (mm.)	12·2	20·2	28·7	30·1	45·0	66·0	91·0
10^4k_1 (sec.$^{-1}$)	9·11	9·21	8·83	9·60	9·29	8·32	8·57
Inhibited reaction at 340·5°.							
p_0 (mm.)	44·0	45·0	50·0	57·0	68·0	70·5	88·0
10^4k_1 (sec.$^{-1}$)	19·0	17·9	17·7	19·2	17·7	18·5	18·8

TABLE 4. *Temperature-dependence.*

Uninhibited						Inhibited					
Temp.	No. of runs	10^4k_1 (sec.$^{-1}$)	Temp.	No. of runs	10^4k_1 (sec.$^{-1}$)	Temp.	No. of runs	10^4k_1 (sec.$^{-1}$)	Temp.	No. of runs	10^4k_1 (sec.$^{-1}$)
361·6°	6	59·7	327·8°	7	9·19	361·6°	6	59·2	327·8°	3	8·34
353·1	6	38·6	324·8	3	7·72	350·8	3	31·7	324·8	5	7·14
345·8	5	25·5	318·8	4	5·64	345·5	4	25·2	318·1	3	4·32
340·5	5	19·5	311·4	6	3·40	340·5	8	18·3	306·3	4	2·07
340·3	2	18·6	298·1	1	1·54	340·3	5	17·8	303·5	5	1·80
335·8	5	14·3				338·8	5	16·1	301·8	3	1·63
						333·3	12	10·9	298·1	7	1·29

means of thin-walled glass tubing. The results are in Table 2. Each observed velocity constant is the mean of five determinations. The calculated values are obtained from the appropriate Arrhenius equations. In view of the large increase in the surface : volume ratio, the reaction is clearly homogeneous.



Effect of cyclo*hexene on the rate of pyrolysis at* 298·1°.

(*p* = *pressure of inhibitor*, p_0 = *pressure of bromide.*

To verify the first-order nature of the decomposition, a number of runs were done with varying initial pressures of *cyclo*pentyl bromide. The first-order constants derived (Table 3) show the first-order nature of the decomposition since in neither case is there a regular trend with initial pressure. For the inhibited runs, p_i/p_0 was at least unity. The effect of added *cyclo*hexene is shown in the Figure, which gives the results of experiments at 298·1°, where the effect is greatest: there is a small but significant decrease from the value in the absence of *cyclo*hexene (1·53 × 10^{-4} sec.$^{-1}$, calculated from the Arrhenius equation, to 1·29 × 10^{-4} sec.$^{-1}$). At the highest temperature of the range studied (361·6°), the difference is much smaller

($59{\cdot}7 \times 10^{-4}$ and $59{\cdot}2 \times 10^{-4}$ sec.$^{-1}$), indicating that the reaction in the presence of *cyclo*hexene had a somewhat greater activation energy than that of *cyclo*pentyl bromide alone.

The variations of the first-order rate constants with temperature shown in Table 4 lead to the Arrhenius equations:

$$\text{Uninhibited;} \quad \log k = 12{\cdot}11 - 41{,}590/2{\cdot}303\boldsymbol{R}T$$

$$\text{Inhibited;} \quad \log k = 12{\cdot}84 - 43{,}700/2{\cdot}303\boldsymbol{R}T$$

The fit is good in both cases.

DISCUSSION

The results described above show that the gas-phase pyrolysis of *cyclo*pentyl bromide in seasoned vessels is a first-order reaction, homogeneous in the absence or presence of *cyclo*hexene. However, in the latter case, at the lowest temperatures used, the rate is lowered some 15% by this addition. The reaction in the presence of *cyclo*hexene can be identified as unimolecular elimination of hydrogen bromide by analogy with decompositions of other bromides studied in the present series. In Part X [5] it will be shown that *cyclo*hexene is a very efficient chain-inhibitor, so the reaction in the absence of *cyclo*hexene may be identified as a mixed unimolecular and chain mechanism, the former predominating. As the reaction proceeds by a mixed mechanism, the Arrhenius parameters are of little fundamental interest. It is worthy of note, however, that the parameters reported by Price *et al.*, namely, $\log A = 11{\cdot}90$ and $E = 41{\cdot}4$ kcal./mole, are in excellent agreement with ours.

The Arrhenius parameters of the secondary bromides so far studied are shown in Table 5. The parameters for *cyclo*pentyl bromide are significantly smaller than the others, though not as small as suggested by Price *et al.* The interpretation of this decrease must await a further discussion of the transition state in gas-phase eliminations.

TABLE 5.

Bromide	log *A*	*E*	Reference
iso-Propyl	13·63	47·8	*a*
sec.-Butyl	13·53	46·5	*b*
*cyclo*Hexyl	13·51	46·1	1
*cyclo*Pentyl	12·84	43·7	This work

a, Maccoll and Thomas, *J.*, 1955, 979. *b*, Kale, Maccoll, and Thomas, unpublished work.

In their paper Price *et al.* show, from their rate constants, at 380°, that the rate of elimination of hydrogen bromide from *cyclo*pentyl bromide is slightly greater than that from *cyclo*hexyl bromide. From a comparison of this rate ratio with that observed for 1-methyl*cyclo*pentyl and 1-methyl*cyclo*hexyl chloride in solution in 80% aqueous alcohol (1 : 125) at 25°,[6] they conclude that "the parallel between the rates of the $S_{\mathrm{N}}1$ reactions and the molecular eliminations breaks down in this case." Further examination of the evidence in the literature demonstrates, as will be shown, that this conclusion is of dubious validity.

In suggesting the analogy between the rates of unimolecular dehydrohalogenation and those of the $S_{\mathrm{N}}1$ and $E1$ reactions in polar solvents, Maccoll and Thomas [7] drew attention to the observed rates of elimination from α- and β-methylated ethyl bromides. Trends observed in these series were qualitatively in accord with those met with in $S_{\mathrm{N}}1$ and $E1$ mechanisms, suggesting that common electronic effects were involved in the two apparently diverse reactions. The argument cannot, of course, be extended to predict quantitative parallelism in rates of reactions which take place at temperatures some 300°

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

[6] Brown and Borkowski, *J. Amer. Chem. Soc.*, 1952, **74**, 1894.

[7] Maccoll and Thomas, *Nature*, 1955, **176**, 392.

apart: no more than a broad qualitative agreement is to be expected. The scope and limitations of the analogy will be discussed in greater detail later.

Studies of unsubstituted *cyclo*alkyl compounds have so far been restricted to the benzenesulphonates and toluene-*p*-sulphonates. There is evidence that these compounds react in polar solvents similarly to the halides. The activation energies (kcal./mole) for *cyclo*pentyl and *cyclo*hexyl compounds are:

	Benzenesulphonate [8]	Toluene-*p*-sulphonate [8, 9, 10]
*cyclo*Pentyl	22·7	24·1, 23·7, 27·6
*cyclo*Hexyl	26·8	27·3, 27·0, 27·4

In addition, the relative rates [8,10] in the two cases (at 50°) are 1 : 20 and 1 : 16. Although for 1-methyl*cyclo*alkyl chlorides the rate ratio is 1 : 125, the activation energies are comparable with those quoted above, namely, 20·8 (1-methyl*cyclo*pentyl) and 24·9 kcal./mole (1-methyl*cyclo*hexyl). In a review, de la Mare [11] concludes with regard to the *cyclo*alkyl toluene-*p*-sulphonates that "the reactivity of *cyclo*pentyl derivatives under ionising conditions is an example of steric acceleration." The much greater rate ratio for 1-methyl*cyclo*alkyl chlorides may thus not unreasonably be ascribed to additional steric acceleration, due to methyl substitution at the seat of reaction. For this reason, the comparison drawn by Price *et al.* is considered unwarranted.

That the results described in this paper conform to, rather than contradict, the proposed analogy can be seen by the following argument. In the first place, the difference in activation energy (2·4 kcal./mole) has the same sign as that for the S_N1 reactions in solution, namely, *cyclo*hexyl > *cyclo*pentyl. This in itself is reasonable evidence, as it is known for the dehydrobromination reaction that the frequency factors are sensibly constant over the series of compounds studied, the major factor influencing the rate being the activation energy. Secondly, the rate ratios for the secondary bromides so far studied (k_{RX}/k_{Pr^iX}), namely:

*iso*Propyl	*sec.*-Butyl	*cyclo*Hexyl	*cyclo*Pentyl
1	2·4	3·2	5·1

at 330° show that, of the *cyclo*alkyl bromides, the *cyclo*hexyl compound more closely resembles the *sec.*-butyl compound in rate. This is also the conclusion drawn by de la Mare [11] from solvolyses of the halides and of the toluene-*p*-sulphonates. Use of 330° in calculating the rate ratios is justified on the grounds that this is the mean temperature of the range experimentally studied, and as such is least likely to suffer from experimental errors in the Arrhenius parameters. Finally, though not much significance can be placed on this because of the long extrapolation, it is of interest that the rate ratio for the gas-phase reactions calculated at 25° is about 1 : 12, a value not dissimilar from those reported for the benzene and toluene-*p*-sulphonates.

The final conclusion to be drawn is that elimination from *cyclo*pentyl and *cyclo*hexyl bromide, far from being an exception to the proposed analogy between gas-phase eliminations and the S_N1 and $E1$ reactions in solution as suggested by Price, Shaw, and Trotman-Dickenson, actually provides further confirmation of a rather striking kind.

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[*Received, June 3rd*, 1957.]

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[8] Brown and Ham, *J. Amer. Chem. Soc.*, 1956, **78**, 2735.

[9] Winstein, Morse, Grunewald, Jones, Corse, Triffan, and Marshall, *ibid.*, 1952, **74**, 1127.

[10] Roberts and Chambers, *ibid.*, 1951, **73**, 5034.

[11] de la Mare, "Progress in Stereochemistry," ed. W. Klyne, Butterworths, London, 1954, Vol. I p. 105.