1007. *Studies in the Pyrolysis of Organic Bromides. Part X.* The Inhibition of the Chain Mode of Decomposition with Special Reference to* n-*Propyl and* n-*Butyl Bromide.*

By ALLAN MACCOLL and P. J. THOMAS.

Olefinic inhibitors are shown to reduce the rate of pyrolysis of *n*-propyl and *n*-butyl bromide. The inhibited rate is independent of the nature, and within limits, of the concentration of the inhibitor. Under conditions of maximum inhibition the decompositions are homogeneous and obey first-order kinetics. It is concluded that the mechanism involved in the decomposition is the unimolecular elimination of hydrogen bromide. The observed rate constants were represented by the Arrhenius equations: †

$$\text{Pr}^{n}\text{Br}: \; k_1 = 7{\cdot}94 \times 10^{12} \exp(-50{,}700/\boldsymbol{R}T) \; (\text{sec.}^{-1})$$

$$\text{Bu}^{n}\text{Br}: \; k_1 = 1{\cdot}51 \times 10^{13} \exp(-50{,}900/\boldsymbol{R}T) \; (\text{sec.}^{-1})$$

in the temperature ranges 350—390° and 370—420° respectively.

INTRODUCTION TO PARTS X—XIII.—In Parts III—IX of the present series the pyrolyses of a number of secondary and tertiary alkyl bromides have been described. The only mechanism which played an appreciable part in the decompositions was the single-stage elimination of hydrogen bromide. In the present paper and those following, the series is extended by the study of the inhibited rate of decomposition of a number of primary alkyl bromides and of certain polybromo-compounds, in which a duality of mechanism is observed, reaction proceeding simultaneously by the unimolecular mechanism and by a radical-chain process. Such behaviour was observed with *n*-propyl bromide.[1] It has been possible to isolate and study the unimolecular process by suppressing the chain decomposition by the use of olefinic inhibitors. Thus it is found that the relative contributions of the two modes of decomposition vary from compound to compound, as does the ease with which the chain component may be inhibited. However, various features have emerged which are common to all the examples studied, and it is thus convenient first to summarise the information obtained as to the relative efficiencies of various inhibitors and the kinetic behaviour in the region of partial inhibitions.

The effect of inhibitor concentration. Most of the exploratory work was carried out on *n*-propyl bromide and the results will be discussed with reference to this compound. Its behaviour is typical, and any significant deviations will be reported when the particular compound is being discussed. Fig. 1 shows a series of pressure–time curves for a constant initial pressure of *n*-propyl bromide in the presence of different concentrations of propene. Also shown is an uninhibited run and one completely inhibited with *cyclo*hexene. With low pressures of propene, a marked sigmoid character develops, which is present in neither the uninhibited nor the completely imhibited runs. In fact, as the propene concentration is increased, there is a steady approach to the smooth curve for a first-order reaction. The same behaviour is shown with *cyclo*hexene, and although the concentrations required to reduce the uninhibited rate and to produce maximum inhibition are smaller, the same limiting curve is obtained.

It is of importance that all the partially inhibited pressure–time curves have at least a common tangent at the origin with the maximally inhibited curve; indeed the time at which the partially inhibited curve leaves the maximally inhibited one increases with inhibitor concentration. The behaviour shown in Fig. 1 may be interpreted on the view that the inhibitor both introduces an induction period and slows down the final rate

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* Part IX, preceding paper.

† The Arrhenius parameters for these two substances have been briefly reported (*J. Chem. Phys.*, 1953, **21**, 178).

[1] Agius and Maccoll, *J.*, 1955, 973.

achieved by the chain reaction. This behaviour is again illustrated in Fig. 2, which shows the first-order plots for the runs illustrated in Fig. 1. With the exception of the uninhibited run, the initial first-order rate coefficients are the same but the deviation from the maximally inhibited line becomes less pronounced as the inhibitor concentration is increased. Although the facile explanation of this behaviour is that it is due to a trace of impurity in the inhibitor which is slowly consumed, this is not regarded as the correct explanation because the behaviour in the region of incomplete inhibition is characteristic of all olefinic inhibitors studied and of all bromides which undergo inhibition. The type of behaviour observed in the presence of inhibitors has one important consequence, that it enables the maximally inhibited reaction to be examined in the initial stages of the decomposition even though chain processes become operative in the later stages. Thus the first-order rate constant may be derived from the initial tangent to the log plot of a partially inhibited reaction. This has proved useful in studying the decomposition of compounds such as *iso*butyl bromide [2] for which the chain mechanism is so strongly developed that it is difficult to suppress it throughout the whole reaction.

FIG. 1. *Pressure–time curves, showing partial inhibition, at constant* p_0 *and with varying* p_i. (*a*) *Uninhibited,* (*b*) 250 *mm. of* iso*pentane,* (*c*) 210 *mm. of propene,* (*d*) 267 *mm. of propene,* (*e*) 336 *mm. of propene,* (*f*) *maximally inhibited,* 350 *mm. of* cyclo*hexene.*

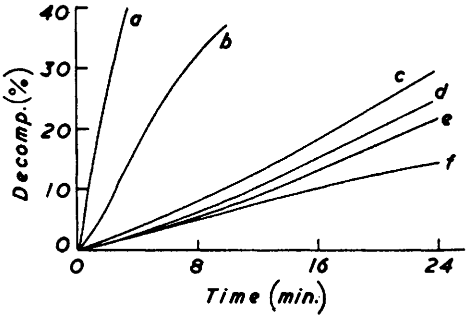
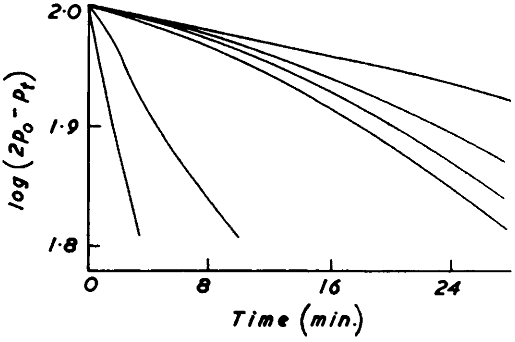


FIG. 2. *First-order plots for the runs illustrated in Fig.* 1.



The constancy of the initial rates in the presence of varying concentrations of inhibitor over a wide range is shown in Fig. 3. The initial rate of decomposition is independent of variations in partial pressure of *cyclo*hexene between 100 and 400 mm. It is not possible, without further work, to account for the broken portion of the curve, that is, to account for the rate as a function of time in the region of incomplete inhibition.

The efficiency of different inhibitors. The results shown in Fig. 3 also enable the important conclusion to be drawn that the *maximally* inhibited rate is independent of the nature of the olefinic inhibitor. However, as is evident from Fig. 1 and has been previously noted,[1] the concentration of propene required to produce maximal inhibition of the decomposition of *n*-propyl bromide was too great to permit an extensive investigation of the residual reaction. The investigation of the process occurring at maximal inhibition for this and for other compounds was thus preceded by a limited investigation of other olefinic substances which were thought to be possible inhibitors. Green and Maccoll's work [3] on *cyclo*hexyl bromide showed *cyclo*hexene to be much more efficient than propene, as well as being stable at 300—400°. Other compounds studied were 2 : 4-dimethylpent-2-ene and *cyclo*pentadiene.

Owing to the complicated kinetics in the region of partial inhibition, the relative efficiencies of different inhibitors cannot be compared very precisely. Table 1 shows the approximate partial pressures of inhibitors which produce the same degree of inhibition

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[2] Unpublished work.

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

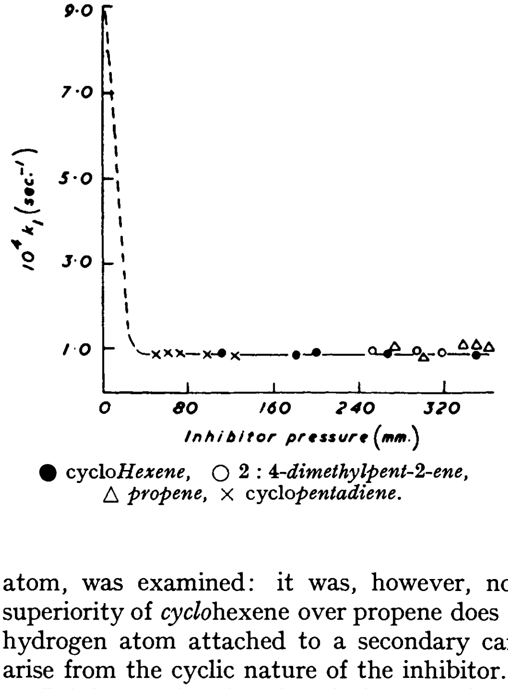
with a constant partial pressure of *n*-propyl bromide. Although *cyclo*pentadiene is more efficient than *cyclo*hexene, the tendency for this compound to dimerise vitiates its use for accurate work, except at very low partial pressures. *cyclo*Hexene is seen to be markedly more efficient than propene.

TABLE 1. *Efficiencies of inhibitors.*

Inhibitor	Propene	2 : 4-Dimethyl pent-2-ene	*cyclo*Hexene	*cyclo*Pentadiene
Pressure (mm.)	500	400	100	40

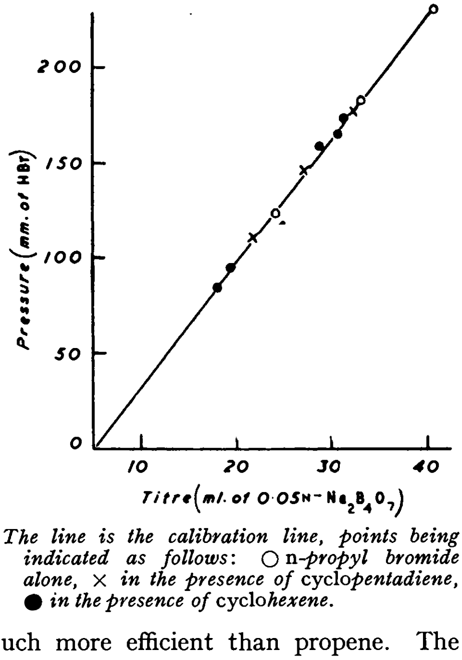
The efficiency of propene is assumed to be due to the stability of the allyl radical formed by abstraction of hydrogen by a bromine atom. A further structural factor might be the strength of the C–H bond concerned. By analogy with alkanes, it might be expected that a hydrogen attached to a tertiary carbon atom would be more readily abstracted, so 2 : 4-dimethylpent-2-ene, which possesses a tertiary allylic hydrogen atom, was examined: it was, however, not much more efficient than propene. The superiority of *cyclo*hexene over propene does not seem to be due to the fact that an allylic hydrogen atom attached to a secondary carbon atom is being attacked: rather must it arise from the cyclic nature of the inhibitor.

FIG. 3. *Maximal inhibition achieved by different inhibitors.*



● cyclo*Hexene*, ○ 2 : 4-*dimethylpent-2-ene*, △ *propene*, × cyclo*pentadiene.*

FIG. 4. *Analytical investigation of* n-*propyl bromide.*



The line is the calibration line, points being indicated as follows: ○ n-*propyl bromide alone,* × *in the presence of* cyclo*pentadiene,* ● *in the presence of* cyclo*hexene.*

It is interesting that the relative ease of inhibition of chains in certain chloro-compounds, *e.g.*, 1 : 2-dichloroethane for which 2 mm. of propene suffice and for which *n*-hexane was quite effective, contrasts strongly with the present observations. Fig. 1 shows a pressure–time curve for the decomposition of *n*-propyl bromide in the presence of an appreciable amount of *iso*pentane. There is initially only a slight induction period, followed by a slight reduction in rate. The explanation of this lies in the large difference in activation energy of one of the chain-propagating steps:

$$\cdot C_nH_{2n}X \longrightarrow C_nH_{2n} + X\cdot$$

A lower limit for the activation energy of such a step can be obtained from thermochemical data.[4] The values in Table 2 are obtained from the heats of formation of the halides given

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[4] Cf. Maccoll and Thomas, *J.*, 1955, 979.

by Mortimer, Pritchard, and Skinner,[5] and the heats of formation of the olefins are taken from an N.B.S. publication.[6] In addition, the primary C–H bond dissociation energy is taken[7] to be 97 kcal./mole, as in ethane. The greater stability of the chloroalkyl radicals renders more probable the chain-ending process:

TABLE 2. *Activation energies (kcal./mole).*

Radical:	C_2H_4X	n-C_3H_6X	*iso*-C_3H_6X
X = Cl	21·6	22·9	25
X = Br	7·2	8·3	10·4

$$\cdot C_nH_{2n}Cl + \text{Inhibitor} \longrightarrow \text{End of chain}$$

which is believed to play very little part in the chain reactions of the bromides.

The results outlined in this section which bear upon the isolation of the unimolecular component of the reaction are as follows. First, the maximally inhibited rate is independent of the nature of the inhibitor. Secondly, it is independent, within wide limits, of the partial pressure of the inhibitor. If now it can be shown that the maximally inhibited rate is of the first order with respect to the bromide, it may be concluded that the unimolecular process is being investigated at maximal inhibition.

EXPERIMENTAL

n-Propyl Bromide.—Commercial *n*-propyl bromide was dried and fractionated, the middle fraction being redistilled and a fraction of constant b. p. and refractive index collected. The sample used for the kinetic work had b. p. 71·2°/763 mm., n_D^{25} 1·4317. Timmermans[8] gives b. p. 71·00°/760 mm., n_D^{25} 1·4318.

It was thought especially important to check that the rate of pressure increase was a measure of the rate of elimination of hydrogen bromide in the presence of inhibitor. Rather than use the technique described in Part II,[1] a method was used for the analytical measurements employing a vapour reservoir. Known amounts of pure hydrogen bromide were admitted into the reaction vessels and the pressure was measured. The hydrogen bromide was then condensed into an evacuated bulb which was sealed off and removed from the vacuum-line. The contents of the bulb were then analysed by breaking the tip under distilled water, washing out the contents, and titrating them against standard borax solution. By repeating this process for varying pressures of hydrogen bromide a graph was constructed relating pressure of hydrogen bromide to the titre of borax solution. After an experiment in which the maximally inhibited decomposition of *n*-propyl bromide was followed by pressure measurements, it was possible to remove the contents of the reaction vessel as described above, and determine the hydrogen bromide pressure in the reaction vessel immediately before its removal. The pressure determined in this way could thus be compared with that calculated from the expression, $p_{HBr} = P_t - p_0 - p_i$ where P_t is the total pressure and p_0 and p_i the initial pressure of the bromide and of the inhibitor respectively. Investigations at 380° are reported in Table 3. It is seen that the two methods agree to within about 1%, so it may be concluded that the stoicheiometry of the reaction even in the presence of an inhibitor may be represented by $C_3H_7Br \longrightarrow C_3H_6 + HBr$. Figure 4 shows the calibration line of pressure against ml. of 0·05N-borax, and the results of the investigation of *n*-propyl bromide.

In order to identify the maximally inhibited reaction with a unimolecular process, it must be demonstrated that the limiting rate is independent of the nature and, within certain limits, the concentration of the inhibitor. To this end, four olefinic inhibitors were employed, propene, 2 : 4-dimethylpent-2-ene, *cyclo*hexene, and *cyclo*pentadiene. With the first two compounds, inhibition was complete only for a very short period at the commencement of the reaction, so the rates could not be determined with the accuracy obtainable with *cyclo*hexene. The results

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[5] Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220.
[6] " Selected Values of the Properties of Hydrocarbons," Nat. Bur. Stand., Washington.
[7] Evans, *Discuss. Faraday Soc.*, 1951, **10**, 112.
[8] Timmermans, " Physicochemical Constants of Pure Organic Compounds," Elsevier, London, 1950.

TABLE 3.

p_{HBr} (press.)	p_{HBr} (anal.)	Reaction (%)	p_{HBr} (press.)	p_{HBr} (anal.)	Reaction (%)	p_{HBr} (press.)	p_{HBr} (anal.)	Reaction (%)
	No inhibitor			With *cyclo*hexene			With *cyclo*pentadiene	
123	123	43·9	94	92	24·1	146	143	46·2
183	181	58·2	158	154	45·0	110	109	32·5
232	231	58·6	106	106	30·1	186	187	44·4
			83	84	23·5			
			165	165	45·3			
			173	169	37·5			
			104	105	22·0			

shown in Table 4 verify the independence of the maximally inhibited rate of the nature of the inhibitor (within the limits of experimental error) and of the concentration over a wide range. The typical log plot in Fig. 5 shows that the first-order rate holds until about 50% decomposition.

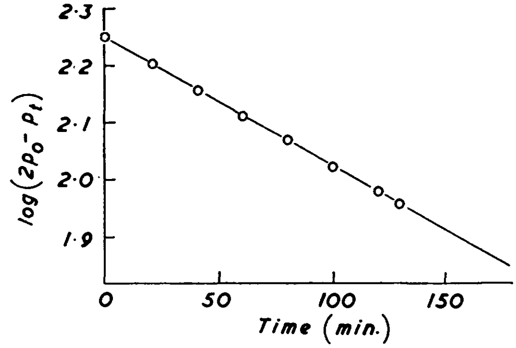


FIG. 5. *Typical first-order plot for the maximally inhibited reaction.*

The first-order nature of the reaction was proved for a wide range of initial pressures at 379°: the first-order rate constant is independent of initial pressure (Fig. 6) in a range 60—500 mm.

The homogeneity of the maximally inhibited reaction was verified by a number of runs done in a packed vessel, the surface : volume ratio being increased roughly five-fold. The results in Table 5 are to be compared with values of $12{\cdot}60 \times 10^{-5}$ sec.$^{-1}$ and $5{\cdot}31 \times 10^{-5}$ sec.$^{-1}$ obtained by means of the Arrhenius equation from the results with an unpacked vessel.

TABLE 4.

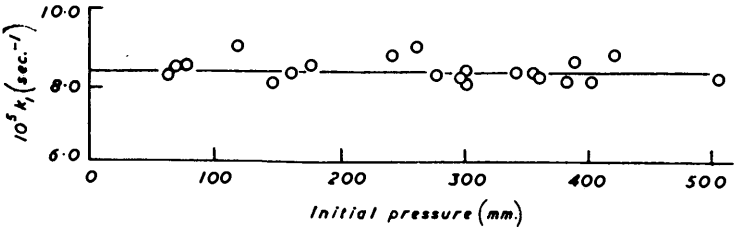
Temp.	p_0 (mm.)	p_i (mm.)	10^3k_1 (sec.$^{-1}$)	10^5k_1 (sec.$^{-1}$; 380°) *	Temp.	p_0 (mm.)	p_i (mm.)	10^3k_1 (sec.$^{-1}$)	10^5k_1 (sec.$^{-1}$; 380°) *
		Propene					cyclo*Hexene*		
380·5	222	360	9·70	9·45	380	302	350	8·75	8·75
379	260	353	8·10	8·75	378·5	295	267	8·04	8·91
379	147	350	9·27	10·0	379	293	200	8·37	9·04
380	215	340	10·2	10·2	379	382	181	8·25	8·91
379·5	134	300	8·00	8·42	380	342	111	8·61	8·61
379	162	270	8·53	9·21	379	352	107	8·45	9·12
	Mean 10^5k = 9·34 sec.$^{-1}$					Mean 10^5k = 9·04 sec.$^{-1}$			
		2 : 4-*Dimethylpent-2-ene*					cyclo*Pentadiene*		
382	175	318	10·15	9·17	380	442	122	8·46	8·46
382	165	295	10·96	9·89	379·5	524	111	8·35	8·79
383	236	25	11·52	9·62	379·5	419	97	8·35	8·79
	Mean 10^5k = 9·56 sec.$^{-1}$				379·3	342	92	8·16	8·59
					379	338	72	8·54	9·23
					378·5	286	60	8·19	9·08
					379	221	50	8·09	8·74
						Mean 10^5k = 8·8 sec.$^{-1}$			

* The correction is made by means of the Arrhenius plot, obtained from the results tabulated below.

Mean first-order rate constants derived from smoothed pressure–time curves, at 350—390°, are shown in Table 6. Only the runs at 390° need comment in this series. As shown in Fig. 7 (a characteristic log plot), the reaction is characterised by a fast start. After an initial rapid period, however, it settles down to reasonable first-order behaviour. The most obvious explanation of this effect is initial incomplete inhibition. It must be emphasised, though, that this effect was not noticeable in the runs at the lower temperatures.

The Arrhenius equation, $k = 7{\cdot}94 \times 10^{12} \exp(-50{,}700/\boldsymbol{R}T)$, was in excellent agreement with the experimental results.

FIG. 6. *Plot of the first-order rate constant as a function of initial pressure.*



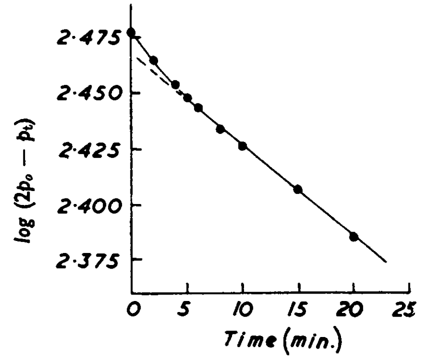


FIG. 7. *Log plot showing the fast start in the case of* n-*propyl bromide in the presence of* cyclo*hexene at* 390°.

n-*Butyl Bromide.*—This was obtained from commercial *n*-butyl bromide and also from commercial *n*-butyl alcohol. The material used in the kinetic runs had b. p. 103·3°/760 mm. (101·6°), n_D^{25} 1·4372 (1·4373), the values in parentheses being Timmerman's.[8] The kinetic behaviour of the two samples was identical.

TABLE 5.

Temp.	p_0 (mm.)	p_i (mm.)	$10^5 k_1$ (sec.$^{-1}$)	Temp.	p_0 (mm.)	p_i (mm.)	$10^5 k$ (sec.$^{-1}$)
385·5°	283	211	12·80	372°	305	229	5·78
385·5	254	258	12·05	372	284	184	5·83
385·5	231	261	12·40	372	194	225	5·44
385·5	194	149	12·40		Mean $10^5 k = 5{\cdot}68$ sec.$^{-1}$		
385·5	170	101	12·70				
385·5	162	220	12·60				
	Mean $10^5 k = 12{\cdot}46$ sec.$^{-1}$						

TABLE 6.

Temp.	350°	360°	370°	379°	390°
No. of runs	4	8	5	13	6
$10^5 k_1$ (sec.$^{-1}$)	1·42	2·72	4·96	8·42	16·7

A comparison of the decomposition calculated from pressure measurements on the basis of the equation, $C_4H_9Br \longrightarrow C_4H_8 + HBr$, with that obtained from a direct determination of the hydrogen bromide produced showed that the equation represented the stoicheiometry of the reaction, both in the presence and in the absence of *cyclo*hexene.

A number of runs at 392° were carried out in the presence of 2 : 4-dimethylpent-2-ene, *cyclo*pentadiene, and *cyclo*hexene, the inhibitor partial pressures being respectively in the ranges

150—250, 50—110, and 100—250 mm. The mean first-order constants were respectively 2·92, 2·68, and 2·73 × 10^{-4} sec.$^{-1}$. As in the case of *n*-propyl bromide, the rate constant with *cyclo*hexene is a little larger than with *cyclo*pentadiene, and smaller than that with 2 : 4-dimethylpent-2-ene. The low rate constant with *cyclo*pentadiene is probably explicable in terms of a dimerisation in the dead space of the apparatus. The experimental evidence demonstrates that the maximally inhibited rate is independent of the nature of the inhibitor. The remainder of the study of the maximally inhibited reaction was done with *cyclo*hexene as the inhibitor.

The lack of dependence of the maximally inhibited rate upon *cyclo*hexene pressure is shown in Table 7. This Table also justifies the use of first-order rate constants, which shows no variation with initial pressure in the range 35—405 mm. Four runs carried out at 371° and at 384°, and six at 400°, gave mean velocity constants of 8·50, 19·4, and 43·8 × 10^{-5} sec.$^{-1}$ respectively. The corresponding values in the unpacked vessel were respectively 8·06, 17·6, and 43·8 × 10^{-5} sec.$^{-1}$. In view of the five-fold increase in the surface : volume ratio, it may be concluded that the reaction is homogeneous.

TABLE 7. *Inhibition by* cyclo*hexene at* 392°.

p_0 (mm.)	p_i (mm.)	10^4k_1 (sec.$^{-1}$)	p_0 (mm.)	p_i (mm.)	10^4k_1 (sec.$^{-1}$)	p_0 (mm.)	p_i (mm.)	10^4k_1 (sec.$^{-1}$)
405	40	2·83	238	87	2·75	102	86	2·76
350	44	2·83	224	94	2·68	57·5	95	2·83
333	78	2·76	183	97	2·68	54·3	88	2·66
306	104	2·75	167	97	2·74	53	87	2·79
305	85	2·76	151	239	2·60	36·5	74	2·63
301	88	2·85	130	80	2·68	35	84	2·94
284	245	2·73	109	94	2·82	35	31	2·84
269	58	2·40						

The results from which the temperature variation of the velocity constant was derived are shown in Table 8. For the runs at 392°, only those for which the initial pressure was between 350 and 151 mm. were used in computing the mean, in order to ensure that the pressure range was comparable at all temperatures. The results in Table 8 were fitted to the equation

TABLE 8.

Temp.	371°	380°	392°	404·5°	418°
No. of runs	4	11	13	6	8
10^5k_1 (sec.$^{-1}$)	8·06	13·8	27·3	56·5	116

$$\log k_1 = 13{\cdot}18 - 50{,}900/2{\cdot}303\boldsymbol{R}T$$

the experimental points lying very close to the theoretical line.

DISCUSSION

The maximally inhibited rates of pyrolysis of *n*-propyl and *n*-butyl bromide have been shown to satisfy the following criteria: (i) The first-order rate constants are independent of the nature of the olefinic inhibitor, of the inhibitor partial pressures over a wide range of pressure, and of the initial pressure of the bromide in the ranges 60—500 and 35—470 mm. respectively. (ii) The reactions are homogeneous. (iii) The rate constants satisfy the Arrhenius equations already given.

It is concluded that these rates pertain to the unimolecular elimination of hydrogen bromide. For *n*-propyl bromide, the parameters of the unimolecular reaction are in marked contrast with those of the uninhibited reaction, namely, $A \sim 10^{11}$ mole$^{-\frac{1}{2}}$ (c.c.)$^{\frac{1}{2}}$ sec.$^{-1}$ and $E \sim 34$ kcal./mole.

The parameters reported here are compared in Table 9 with those for the corresponding chlorides.[9]. R represents the ratio of the rates (Bu^n/Pr^n) at the temperature indicated, which was chosen so that the rate constants of the compounds were of the same order of magnitude. It will be seen that, despite the differences in the parameters of the Arrhenius equations, the rate ratios of the two compounds are very similar.

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[9] Barton, Head, and Williams, *J.*, 1951, 2039.

TABLE 9.

	Chloride			Bromide		
Alkyl	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	R (440°)	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	R (370°)
Pr^n	2·83	55·0	—	0·79	50·7	—
Bu^n	10	57·0	1·3	1·51	50·9	1·5

After our work was completed, Blades and Murphy[10] reported results for *n*-propyl bromide in excellent agreement with it. They used toluene as carrier gas, in a flow technique similar to that developed by Szwarc.[11] In the temperature range 500—600° the rate was:

$$k_1 = 1{\cdot}0 \times 10^{13} \exp(-50{,}700/\boldsymbol{R}T)$$

substantiating our values. This is the more impressive since the present work was done at about 100° lower. The fact that Blades and Murphy could detect no dibenzyl in their experiments is explicable in terms of the activation energies of the inhibited free-radical and unimolecular mechanisms: in the temperature range considered, the rate of the former would be relatively very small.

Recently, also, Semenov, Sergeev, and Kapralova[12] reported an investigation of the pyrolysis of *n*- and *iso*-propyl bromide. For the latter they found:

$$\log k_1 = 12{\cdot}74 - 47{,}000/2{\cdot}303\boldsymbol{R}T$$

They confirmed the first-order, unimolecular character of the reaction, and the rate constants are in reasonable agreement with those given by Thomas and Maccoll[13] and Blades and Murphy.[14] However, for *n*-propyl bromide they reported that the reaction was of order 1·5, in agreement with Agius and Maccoll,[15] and that the rate constant could be represented by

$$\log k_{1{\cdot}5} = 9{\cdot}58 - 42{,}000/2{\cdot}303\boldsymbol{R}T$$

with $k_{1{\cdot}5}$ in units of mm.$^{-\frac{1}{2}}$ sec.$^{-1}$. Changing to units of mole$^{-\frac{1}{2}}$ c.c.$^{\frac{1}{2}}$ sec.$^{-1}$, by conversion of the calculated rate constants at 300° and 350° into these units gives:

$$\log k_{1{\cdot}5} = 13{\cdot}62 - 42{,}700/2{\cdot}303\boldsymbol{R}T$$

which is to be compared with Agius and Maccoll's equation namely

$$\log k_{1{\cdot}5} = 10{\cdot}86 - 33{,}800/2{\cdot}303\boldsymbol{R}T$$

The temperature range investigated by Semenov *et al.* was 350—500°, which is to be compared with 300—380° studied by Agius and Maccoll. Although at first sight there appears to be a marked divergence between the rate equations, the maximum ratio of the rates in the overlapping temperature range is 2. As Semenov *et al.* point out, air was not rigorously excluded from Agius and Maccoll's apparatus, so possibly the coating on the walls of the vessel was oxidised, allowing heterogeneous catalysis. It should be pointed out that reproducibility in chain decompositions is very much more difficult to obtain than in reactions proceeding by a unimolecular mechanism.

The question as to the essential nature of the difference in pyrolytic behaviour of *n*- and *iso*-propyl bromide has been further discussed by Semenov.[16] Independently, he arrived at almost the same explanation as Maccoll and Thomas,[17] in terms of propagating

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[10] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.

[11] Szwarc, *J. Chem. Phys.*, 1949, **17**, 432.

[12] Semenov, Sergeev, and Kapralova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 301.

[13] Maccoll and Thomas, *J. Chem. Phys.*, 1951, **19**, 977; *J.*, 1955, 979.

[14] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.

[15] Agius and Maccoll, *J.*, 1955, 973.

[16] Semenov, " On a Number of Problems of Chain Reactions and Chemical Kinetics," Moscow, 1954.

[17] Thomas, Thesis, London, 1953; Maccoll and Thomas, *J.*, 1955, 979.

and stopping radicals. The only point of variance is the nature of the chain-ending step. Semenov favours $2CH_3{\cdot}CH_2{\cdot}CHBr{\cdot} \longrightarrow$ End of chain, whereas Maccoll and Thomas postulated ${\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + Br \longrightarrow$ End of chain. Further work will be required before it is possible unambiguously to decide between the two mechanisms.

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