Studies in the Pyrolysis of Organic Bromides. Part V. The Pyrolysis of* cyclo*Hexyl Bromide.*†

By J. H. S. Green and Allan Maccoll.

[Reprint Order No. 5996.]

From 300° to 350°, in seasoned vessels, *cyclo*hexyl bromide decomposes homogeneously in the gaseous phase into *cyclo*hexene and hydrogen bromide according to a first-order law. Departures from this law after about 40% decomposition have been attributed to the incursion of the back-reaction. Rate constants for the initial stages of the reaction were fitted to the expression $k_1 = 3{\cdot}24 \times 10^{13} \exp(-46{,}100/RT)$ (sec.$^{-1}$). On the basis of this evidence and of the inability of *cyclo*hexene to inhibit the reaction, the mechanism is identified as unimolecular elimination of hydrogen bromide. No significant decrease in the rate constants with decreasing initial pressure was observed in the range 400—40 mm.

No previous studies have been made of the kinetics of pyrolysis of *cyclo*hexyl bromide in the gaseous phase. This compound was of interest to the present series of investigations as both the C–H and the C–Br bonds to be broken in the elimination of hydrogen bromide occur in secondary groups (cf. *sec.*-butyl bromide, Part IV *). It is also of interest to see the effect of the cyclic structure upon the rate. By analogy with the secondary bromides already studied, it might be expected that *cyclo*hexyl bromide would decompose cleanly into *cyclo*hexene and hydrogen bromide by a unimolecular reaction.

EXPERIMENTAL

*cyclo*Hexyl bromide (commercial) was freed from the alcohol by shaking with 60% aqueous hydrogen bromide, the excess of acid was then removed, and the sample dried and fractionated under a vacuum. It then had b. p. 72°/29 mm., n_D^{25} 1·4934 [cf. b. p. 71—72°/32 mm. (Beilstein's "Handbuch"), n_D^{25} 1·4935 (Heston, Hennelly, and Smythe, *J. Amer. Chem. Soc.*, 1950, **72**, 2071)].

A commercial sample of *cyclo*hexene was shaken with portions of aqueous ferrous sulphate to remove peroxides until no further change occurred. It was then washed with water, dried ($CaCl_2$), and fractionated at atmospheric pressure. It was stored in the dark over solid potassium hydroxide. It had b. p. 82·0°, n_D^{25} 1·4439 [cf. b. p. 82·3° (Pink and Ubbelohde, *Trans. Faraday Soc.*, 1948, **44**, 710), 83° (Timmermanns, "Physical Constants of Pure Organic Compounds," Elsevier, 1950), n_D^{25} 1·4437 (*op. cit.*)]. Analysis, by a method to be described later, showed it to be at least 99·2% pure.

Stoicheiometry of the Reaction.—Confirming the analogy with previous work on the alkyl bromides, it was verified that the products of pyrolysis were *cyclo*hexene and hydrogen bromide, and the reaction was conveniently measurable at 300° in a clean-walled reaction vessel. The ratio of final to initial pressure was always less than the value of 2 predicted from (1), owing to equilibrium between *cyclo*hexyl bromide and its decomposition products. The reaction appeared to be fairly clean, insofar as all the gases produced were condensed at liquid air temperatures. If the reaction is

$$C_6H_{11}Br \longrightarrow C_6H_{10} + HBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

then the amount of decomposition can be obtained from a knowledge of the initial pressure (p_0) and the pressure at time t (p_t)

$$\text{Decomposition (\%)} = 100\,(p_t - p_0)/p_0$$

This value can be compared with that obtained by direct titration of the hydrogen bromide produced.

The analytical procedure was varied slightly from that described in Part I (*J.*, 1955, 965). A known weight of *cyclo*hexyl bromide was introduced into the reaction vessel and after a given

---

* Part IV, preceding paper. † A preliminary report of the Arrhenius parameters for this reaction has already been given (*J. Chem. Phys.*, 1953, **21**, 178).

time the total pressure was noted and the products were condensed under a vacuum into a tube of *ca.* 200 c.c. capacity and sealed off. The tip of the tube was then broken under standard alkali and titrated as described previously. The results of such an investigation are shown in Fig. 1, in which the percentage decomposition found from an analysis for acid produced is plotted against that obtained from pressure measurements. The points all lie close to the line of unit slope, as would be expected from equation (1).

It was thought desirable to investigate the *cyclo*hexene–hydrogen bromide ratio, by analysis for both constituents in a single run. The *cyclo*hexene was estimated by bromine absorption, the most satisfactory results being obtained by the use of standard bromate–bromide. The procedure used was essentially that of Mulliken and Wakeman (*Ind. Eng. Chem., Anal.*, 1935, **7**, 59) who recorded that it tended to give low results. This observation was confirmed by Lucas and Pressman (*ibid.*, 1938, **10**, 140), who developed a technique with added mercuric sulphate which, however, in the case of *cyclo*hexene, did not appear to improve the results. Typical results were : *cyclo*hexene taken 0·1042, 0·0845 g. ; found 0·1033, 0·0839 g. For the analysis of *cyclo*hexene from the kinetic runs, the solution of the olefin in carbon tetrachloride was added to the bromate–bromide solution and the usual procedure followed. The results are shown in Table 1.

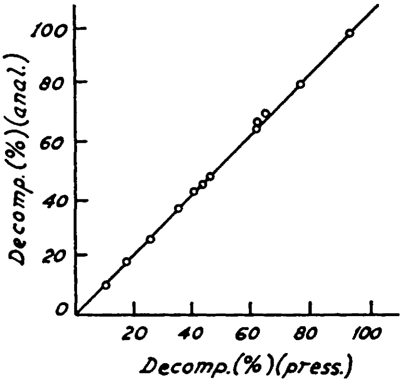


FIG. 1. *Percentage decomposition determined from pressure measurements and from a direct determination of the hydrogen bromide produced.*

TABLE 1.

Temp.	295°	335°	327°	345°	323° *	355° *
Decomp. (%)	25·3	45·5	63·1	78·3	66·0	97·0, 98·0
C_6H_{10} : HBr	0·96	1·02	1·04	0·98	0·96	1·06, 0·98

* Sealed-tube technique.

The results presented in Fig. 1 and Table 1 give reasonable proof of the stoicheiometry represented by (1).

Independent evidence of the stability of *cyclo*hexene at the temperature used comes from the work of Küchler (*Nach. Akad. Wiss. Göttingen, Math.-phys. Kl.*, 1939, **1**, 231) who studied the decomposition and showed it to be

$$C_6H_{10} \longrightarrow C_4H_6 + C_2H_4.$$

This reaction is the reverse of a diene synthesis. The first-order rate constant was expressed as $k = 9{\cdot}0 \times 10^{12} \exp(-57{,}500/\boldsymbol{R}T)$ (sec.$^{-1}$). At 350° this gives a half-life of 100 days. Rowley and Steiner (*Discuss. Faraday Soc.*, 1951, **10**, 198) suggest that the activation energy may even be as high as 64 kcal. So the secondary decomposition of *cyclo*hexene may be ignored in the present work.

RESULTS

The reaction was studied by measuring the rate of pressure increase as described in Part I (*loc. cit.*). It was found to follow a first-order law up to about 40% decomposition, the first-order constants being independent of initial pressure. As the reaction proceeded, the first-order constants fell, which can be ascribed to the reverse reaction, $C_6H_{10} + HBr \longrightarrow C_6H_{11}Br$. Preliminary runs in a clean-walled reaction vessel gave highly irreproducible results. In particular, traces of oxygen catalysed the reaction. On careful exclusion of oxygen, a gradual decrease in rate was observed. Thus in six runs at 304° the first-order constant dropped from $4{\cdot}3 \times 10^{-4}$ to $2{\cdot}2 \times 10^{-4}$ (sec.$^{-1}$). When the vessel was " seasoned " with the products of pyrolysis of allyl bromide (Part II, *J.*, 1955, 973) the rate dropped to $1·13 \times 10^{-4}$ sec.$^{-1}$, and the behaviour of *cyclo*hexyl bromide became reproducible.

To test the homogeneity of the reaction under these conditions, the surface : volume ratio was increased by a factor of about three, and no significant change in the rate was observed (see Table 2). Within the limits of experimental error the reaction is essentially homogeneous.

TABLE 2. *Effect of surface : volume ratio.*

Temp.	304°	309·5°	347·7°	349·4°
Surface : vol., 1·07 (cm.$^{-1}$) : 10^4k (sec.$^{-1}$)	1·17	1·62, 1·69	18·6	20·6
Surface : vol., 2·83 (cm.$^{-1}$) : 10^4k (sec.$^{-1}$)	1·10	1·76, 1·71	18·9	19·1

The lack of dependence of the first-order rate constants on initial pressure is illustrated for a series of runs at 327° in Table 3.

TABLE 3. *Effect of initial pressure, at* 327°.

p_0 (mm.)	435	362	333	275	247	245	203
10^4k_1 (sec.$^{-1}$)	5·04	5·34	4·90	4·65	4·73	5·26	4·93
p_0 (mm.)	195	165	134	80	75	64	40
10^4k_1 (sec.$^{-1}$)	4·81	5·44	5·42	5·50	4·60	5·38	5·60

The temperature dependence of the rate constant, determined from the means of a number of runs, is shown in Table 4. The variation of the rate constant with temperature was fitted to the Arrhenius equation $k_1 = 2·4 \times 10^{13} \exp(-46,100/\boldsymbol{R}T)$ (sec.$^{-1}$), the results being shown graphically in Fig. 2.

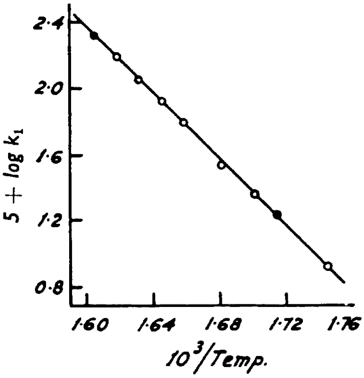


FIG. 2. *The Arrhenius plot. Black circles indicate runs in a packed vessel.*

In order to identify the mechanism, the decomposition was carried out in the presence of a number of added substances. *cyclo*Hexene should be a powerful inhibitor of chain reactions by virtue of the four C–H bonds adjacent to the double bond, the removal of any one of which would lead to a *cyclo*hexenyl radical. This should be comparable in stability to an allyl radical formed from propene and should readily remove bromine; so if bromine atom chains were present, inhibition should result. That no such inhibition results is shown in Table 5 (the calculated figures are obtained from the Arrhenius equation), and is definite evidence in view of the fact that P. J. Thomas (personal communication) has shown that *cyclo*hexene strongly

TABLE 4. *Temperature dependence.*

Temp.	350°	345°	340°	335°	330°	327°	322°	320°	315°	310°	300°
No. of runs	3 *	3	1	7	4	14	7	1	5	1 *	4
10^4k_1 (sec.$^{-1}$)	21·83	15·67	11·48	8·57	6·44	5·11	3·59	3·23	2·34	1·76	0·89

* In a packed vessel.

TABLE 5. *Effect of added* cyclo*hexene.*

			10^4k_1 (sec.$^{-1}$)					10^4k_1 (sec.$^{-1}$)	
Temp.	p_0 (mm.)	$p_{C_6H_{10}}$ (mm.)	obs.	calc.	Temp.	p_0 (mm.)	$p_{C_6H_{10}}$ (mm.)	obs.	calc.
313°	191	57	2·17	2·09	319·5°	230	264	3·30	3·22
316·8	175	52	2·84	2·72	324·5	217	139	4·33	4·47
316·8	228	145	2·42	2·72	326	192	123	4·68	4·92
317·2	201	129	2·57	2·76	326	217	251	4·92	4·92

inhibits the pyrolysis of *n*-propyl bromide which has been shown (Part II, *loc. cit.*) to decompose according to a chain mechanism.

Since allyl bromide was used for producing seasoned walls, it was desirable to ascertain whether the addition of allyl bromide had an effect on the rate. At the temperature shown, allyl bromide decomposes with a half-life of about 150 min., whereas *cyclo*hexyl bromide has a half-life of about 20 min. The results are set out in Table 6 (calculated values from the Arrhenius plot). The course of the reaction was unchanged by the presence of allyl bromide and the first-order rate constants were essentially unaltered.

TABLE 6. *Rate constants in presence of allyl bromide* (15 mm.).

Temp.	330°	328°	328°	328°
p_0 (mm.)	220	308	245	325
10^4k_1 (sec.$^{-1}$) obs.	6·53	5·38	4·97	5·16
10^4k_1 (sec.$^{-1}$) calc.	6·57	5·72	5·72	5·72

FIG. 3.

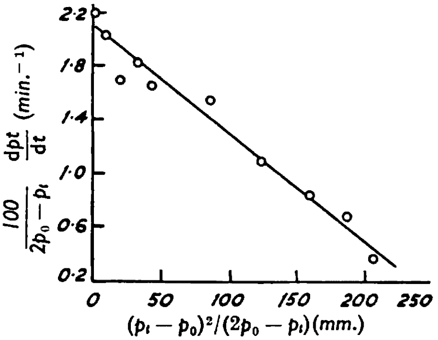
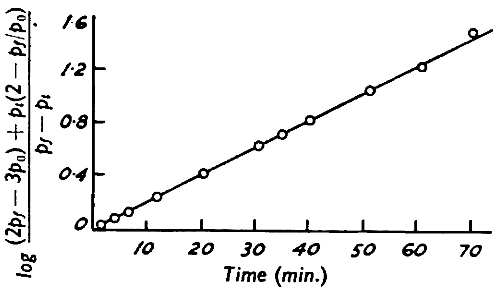


FIG. 4.



Interpretation of the results in terms of a combination of forward and reverse reactions: (FIG. 3, *method A*) (FIG. 4, *method B*).

It might be expected that bromine would accelerate a reaction proceeding by a bromine-atom chain mechanism and might even be capable of initiating such a route. For this reason some runs were done at 313·4° in the presence of varying pressures of bromine (see Table 7).

TABLE 7. *Effect of added bromine.*

p_0 (mm.)	163	251	140
p_{Br_2} (mm.)	6	13	30
10^4k_1 (sec.$^{-1}$)	2·1	1·89	2·59

The rate constant calculated from the Arrhenius plot for this temperature is 2·14 × 10^{-4} sec.$^{-1}$. Thus small pressures of bromine are without effect on the rate of decomposition of *cyclo*hexyl bromide. This result is paralleled by observations on *tert.*-butyl bromide (following paper).

During the work considerable qualitative evidence accumulated that the reaction did not go to completion. First, the values of p_f/p_0 were always less than the value 2 demanded by the reaction, $C_6H_{11}Br \longrightarrow C_6H_{10} + HBr$ (p_f = final pressure). Secondly, the logarithmic plots for the first-order rate constants deviated from a straight line to an extent dependent on pressure and temperature, the effect being more marked at high pressures and low temperatures. Thirdly, in the presence of added *cyclo*hexene, the deviations from linearity increased as the pressure of *cyclo*hexene increased. That the data are consistent with the scheme $C_6H_{11}Br \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_{10} + HBr$ can be seen by applying the complete kinetic equation in either of two ways: in the differential form

$$(A) \qquad -\frac{1}{2p_0 - p_t} \cdot \frac{dp_t}{dt} = k_1 - k_2\frac{(p_t - p_0)^2}{(2p_0 - p_t)}$$

or in the integrated form

$$(B) \qquad k_1 = \frac{p_f - p_0}{t(3p_0 - p_f)} \ln \frac{(2p_f - 3p_0) + p_t\,(2 - p_f/p_0)}{p_f - p_t}$$

p_0 is the initial pressure of *cyclo*hexyl bromide, p_t the total pressure at time t, and p_f the final pressure.

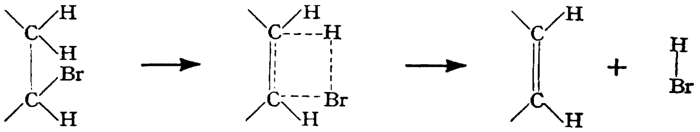
In method (*A*), $(2p_0 - p_t)^{-1}dp_t/dt$ was plotted against $(p_t - p_0)^2/(2p_0 - p_t)$, giving a straight line of slope k_2 and intercept k_1. This is shown in Fig. 3, the value of k_1 thus determined being $3{\cdot}5 \times 10^{-4}$ sec.$^{-1}$. k_1 is derived by method (*B*) from a plot of $\log\{[(2p_f - 3p_0) + p_t\,(2 - p_f/p_0)]/(p_f - p_t)\}$ against t, as shown in Fig. 4. The corresponding value of k_1 is $3{\cdot}78 \times 10^{-4}$ sec.$^{-1}$. These two values are to be compared with the value $3{\cdot}53 \times 10^{-4}$ sec.$^{-1}$ obtained from the initial slope of the conventional first-order plot. In both methods (*A*) and (*B*) the straight lines are reasonably good. Because of dead-space errors, it is not considered that reliable values of K_p could be derived from experiments in the present apparatus. It can, however, be concluded that the experimental results are in accord with an equilibrium between *cyclo*hexyl bromide and its decomposition products, lying well towards dissociation in the temperature range 300—350°.

DISCUSSION

It has been established that the decomposition of *cyclo*hexyl bromide in the temperature range 300—350° proceeds homogeneously according to the scheme

$$C_6H_{11}Br \longrightarrow C_6H_{10} + Br$$

The reaction is of the first order and no pressure dependence of the constants has been observed in the pressure range 40—400 mm. *cyclo*Hexene has no effect on the rate; bromine very little. These facts can be interpreted on the basis of the mechanism *not* involving bromine atom chains; further such chains seem very difficult to induce. In view of the magnitude of the activation energy, the bromine-atom non-chain mechanism suggested for ethyl bromide by Daniels and Veltman (*J. Chem. Phys.*, 1939, **7**, 756) and found by one of us for allyl bromide (Part I, *loc. cit.*) is eliminated as this leads to an activation energy equal to the C–Br bond strength (~60 kcal.). The remaining possibility is the unimolecular elimination of hydrogen bromide through a four-centre transition state:



The value of the activation energy found in the present work is 46·1 kcal., to be compared with the values 47·8 and 43·8 kcal. for *sec.*-propyl and *sec.*-butyl bromide respectively (Parts III and IV, *J.*, 1955, 979, 2445). In all these cases the elimination proceeds by the breaking of C–H and C–Br bonds in secondary groups.

The observed value of the frequency factor ($2{\cdot}4 \times 10^{13}$ sec.$^{-1}$) is close to that found for a large number of unimolecular reactions (~10^{13}). Although a number of workers (for references see Slater, *Proc. Roy. Soc.*, 1948, *A*, **194**, 112) have shown that the frequency

TABLE 8.

Halide	log *A*	*E* (kcal.)	Ref.
	Elimination of hydrogen bromide.		
sec.-Propyl	13·62	47·8	Part III
sec.-Butyl	12·63	43·8	„ IV
tert.-Butyl	13·3	40·5	K. & S.*
„	14·00	42·2	Part VI
*cyclo*Hexyl	13·38	46·1	This work
	Elimination of hydrogen chloride.		
Ethyl	14·6	60·8	1
n-Propyl	13·5	55·0	2
sec.-Propyl	13·4	50·5	3
n-Butyl	14·0	57·0	2
tert.-Butyl	13·9, 12·4	45·0, 41·4	4, 5

* Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.

[1] Barton and Howlett, *J.*, 1949, 155. [2] Barton, Head, and Williams, *J.*, 1951, 2039. [3] Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114. [4] Brearly, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 44. [5] Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

factor should be of the order of 10^{13} when a single bond breaks, the extension of the argument to the four-centre case is not immediately obvious. In fact Glasstone, Laidler, and Eyring (" Theory of Rate Processes," McGraw-Hill, New York, 1941) have suggested that in this type of reaction the frequency factor should be low, corresponding to a higher degree of organisation in the transition state. This view is certainly not borne out in elimination reactions involving the formation of a double bond, as Table 8 shows. It may be that, because of restricted rotation in the initial state, the change in the degree of organisation on going to the transition state is slight.

The authors acknowledge their indebtedness to Professor C. K. Ingold, F.R.S., for his interest, and to Dr. P. J. Thomas for many discussions. One of them (J. H. S. G.) acknowledges the award of a D.S.I.R. Maintenance Grant.

William Ramsay and Ralph Forster Laboratories, University College,
Gower Street, London, W.C.1. [*Received, December 22nd,* 1954.]