902. *The Kinetics of the Pyrolysis of Cyclopentyl Chloride.*

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In " seasoned " reaction vessels gaseous cyclopentyl chloride decomposes in the range 309—376° by a nearly homogeneous first-order reaction to give cyclopentene and hydrogen chloride. The presence of cyclohexene does not affect the rate, and bromine causes only a slight acceleration. The rate is expressible as $k_1 = 10^{13\cdot47} \exp(-48{,}300/\boldsymbol{R}T)$ (sec.$^{-1}$) and there is no variation in rate coefficient over the initial pressure range 40—400 mm. The results are consistent with a unimolecular elimination of hydrogen chloride. The faster rate compared with those of cyclohexyl chloride and s-butyl chloride is attributed to steric acceleration.

In polar solvents cyclopentyl compounds undergo solvolysis and elimination reactions more rapidly than do the corresponding cyclohexyl compounds.[1] In view of the proposed analogy between the rates of unimolecular pyrolysis of alkyl halides in the gas phase and the S_N1 or $E1$ reactions in solutions,[2] the present investigation was undertaken to determine whether this analogy was maintained for the gas-phase dehydrochlorination of cyclopentyl and cyclohexyl chloride.

In a previous paper[3] cyclohexyl chloride was shown to decompose in the range 318—385° to cyclohexene and hydrogen chloride by a homogeneous unimolecular mechanism. No previous study of the pyrolysis of cyclopentyl chloride has been reported, although the kinetics of the gas-phase dehydrobromination of cyclohexyl[4] and cyclopentyl[5] bromide have been investigated by other workers.

Experimental

Cyclopentyl chloride, prepared from cyclopentanol and zinc chloride–hydrochloric acid, was shaken in turn with concentrated sulphuric acid, saturated sodium hydrogen carbonate solution, and potassium chloride solution, dried ($CaCl_2$), fractionally distilled, and collected at b. p. 113·5°/760 mm. It had n_D^{25} 1·4489 (lit.,[6] 113°/760 mm., n_D^{25} 1·4490 (Found: C, 57·5; H, 8·7; Cl, 34·2. Calc. for C_5H_9Cl: C, 57·4; H, 8·7; Cl, 33·9%).

Cyclopentene, freshly distilled from 85% phosphoric acid–cyclopentanol, was washed with calcium chloride solution, dried ($CaCl_2$), and fractionally distilled. It had b. p. 44·4°/760 mm. (lit.,[7] 44·4°/760 mm.).

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[1] Brown, Fletcher, and Johannesen, *J. Amer. Chem. Soc.*, 1951, **73**, 212; Brown and Ham, *ibid.*, 1956, **78**, 2735; Roberts and Chambers, *ibid.*, 1951, **73**, 5034; Winstein, Morse, Grunwald, Jones, Corse, Trifam, and Marshall, *ibid.*, 1952, **74**, 1127.

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

[3] Swinbourne, *Austral. J. Chem.*, 1958, **11**, 314.

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

[5] Price, Shaw, and Trotman-Dickenson, *J.*, 1956, 3855; Kale and Maccoll, *J.*, 1957, 5020.

[6] Roberts and Chambers, *J. Amer. Chem. Soc.*, 1951, **73**, 5030.

[7] Egloff, " Physical Constants of Hydrocarbons," Reinhold, New York, 1940, Vol. II, p. 306.

The purification of cyclohexene has been described elsewhere.[3]

The decompositions were carried out in a Pyrex glass vessel (~350 ml.) housed in a metal-block thermostat which was heated electrically and controlled to ±0·1° with a Sunvic controller type RT2. Temperatures were measured with a chromel–alumel thermocouple calibrated against a rare-metal couple which had been checked by the National Standards Laboratory, Sydney, and were considered accurate within ±0·5°. The reaction vessel was connected to a high-vacuum system and reagents were introduced from vapour reservoirs. Parts of the reaction system external to the furnace, and vacuum-lines used for handling condensable materials, were heated with electrical resistance wire. After the vessel had been "seasoned" with the pyrolysis products of allyl bromide, the decomposition of cyclopentyl chloride was followed by measuring the rate of pressure increase, a glass-membrane gauge of the type described by Mouquin and Garman [8] and Newton [9] being used. Care was taken to exclude even traces of oxygen as these were found to have an accelerating effect. The membrane gauge, which was used as a null-point detector, consisted of two chambers separated by a thin glass diaphragm silver-coated on the balancing side. A galvanometer lamp was focused upon the silver surface, and the reflected image of the cross-hairs viewed on a ground screen: deviation from the point of balance could be detected by both movement of and decrease in clarity of the image. Several gauges were constructed which had a sensitivity of ~0·1 mm., and could withstand 1 atm. differential pressure.

As a check on the stoicheiometry, decompositions were carried out until no further increase in pressure was detectable. In all cases, the final pressure (p_f) was almost twice the initial pressure (p_0) as shown in Table 1.

TABLE 1. *Ratio of final to initial pressure.*

Temp. (°c)	376·1	358·6	358·5	341·7	341·7	341·6	325·3	325·0	309·6
p_0 (mm.)	95·0	52·4	150·5	54·8	156·8	87·4	222·9	209·4	100·7
p_f/p_0	1·99	1·94	1·96	1·97	1·99	1·96	1·98	1·96	1·98
Time (hr.)	18	26	7	19	48	21	45	21	91

There was also good agreement between the extent of decomposition as predicted from pressure measurements and from titration of the hydrogen chloride formed. In a series of runs the contents of the reaction vessel were rapidly condensed into a phial containing a small amount of distilled water cooled in liquid air. (There were no noticeable quantities of non-condensable material.) The contents of the phial were added to distilled water and titrated with standard alkali (Table 2).

TABLE 2. *Agreement between pressure change and hydrogen chloride analysis.*

Temp.	309·0°	309·0°	309·0°	325·0°	325·0°	341·9°	341·7°
p_0 (mm.)	219·3	442·8	203·8	210·9	213·5	249·0	156·8
Decompn. (%) (press.)	66·9	16·2	96·4	26·7	79·1	49·1	99·4
,, (anal.)	66·6	16·5	97·1	27·2	78·9	50·8	98·8

Cyclopentene was identified as the main organic pyrolysis product by means of its infrared absorption spectrum.* The products of a run approaching complete decomposition were collected in a phial cooled in liquid air, and the sample was warmed to room temperature. The infrared spectrum (3500—650 cm.$^{-1}$) immediately obtained compared almost identically with that of a sample of pure cyclopentene to which a trace of silicone grease (used as stopcock lubricant) had been added.

The stability of cyclopentene was tested by heating this substance alone in a seasoned reaction vessel at 376° for 52 hr. During this time the pressure increased only from 142·2 to 144·2 mm. Vanas and Walters [10] identified cyclopentadiene and hydrogen as the main pyrolysis products from cyclopentene. The first-order rate coefficient for the decomposition was expressed as $k_1 = 1{\cdot}10 \times 10^{13} \exp(-58{,}800/\boldsymbol{R}T)$ (sec.$^{-1}$) which gives a half-life of 46 days at 376° compared with 7 min. for cyclopentyl chloride at the same temperature. The secondary decomposition may therefore be ignored in the present work.

Kinetic Results.—For kinetic runs over the range 309—376°, the rate of pressure increase

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* The author is indebted to Mr. I. Reece for these analyses.

[8] Mouquin and Garman, *Ind. Eng. Chem., Analyt.*, 1937, **9**, 287.

[9] Newton, *J. Chem. Phys.*, 1950, **18**, 797.

[10] Vanas and Walters, *J. Amer. Chem. Soc.*, 1948, **70**, 4035.

closely followed the first-order law, $k_1t = \ln\,[p_0/(2p_0 - p)]$ to at least 75% decomposition, and no induction period was apparent. At a given temperature, the rate coefficient showed no significant variation with changes in the initial pressure of cyclopentyl chloride from 40 to 400 mm., and the rate of decomposition was not affected by the presence of large quantities of cyclohexene (an efficient inhibitor of radical-chain reactions [11]); k_1 was estimated from the slope of the graph of log $(2p_0 - p)$ against t (" orthodox " method) and by Guggenheim's method.[12] There was good agreement between the two sets of values so obtained, provided Allen's correction [13] was applied for 2% " dead-space " in the reaction system. (p_0 was estimated by direct extrapolation to zero time [14] or indirectly from p_∞ in the case of kinetic runs for which the theoretical starting time of the reaction was not accurately known.) Reaction rate coefficients for cyclopentyl chloride decomposition at 342° with and without added cyclohexene are shown in Table 3, which is typical of results also obtained at other temperatures. These are summarised in Table 4 as mean rate coefficients with 90% confidence limits of the mean (runs with and without inhibitor have been combined).

TABLE 3. *Decompositions at* 342°.

p_0 (mm.)	53	65	87	105	202	298	420	53 [h1]	158 [h2]
10^5k_1 (sec.$^{-1}$) (orth.)	20·5	20·9	19·5	20·3	21·1	20·7	20·6	19·9	20·6
10^5k_1 (sec.$^{-1}$) (Gugg.)	—	21·7	20·7	22·2	22·7	21·6	20·4	20·3	19·9

[h1] Decomposition in presence of 103 mm. of cyclohexene.
[h2] Decomposition in presence of 101 mm. of cyclohexene.

TABLE 4. *The temperature dependence of rate coefficient.*

Temp.	309°	326°	342°	359°	376°
10^5k_1 (sec.$^{-1}$)	2·21 ± 0·06	7·02 ± 0·28	20·8 ± 0·4	59·7 ± 1·1	162·8 ± 1·8
No. of runs	10	6	9	7	10

The constants in the Arrhenius equation, $k_1 = A \exp(-E/\boldsymbol{R}T)$, were estimated from the best straight line of log k_1 plotted against $1/T$ by the least-squares procedure. The same statistical weight was given to each individual run and it was assumed that all errors resided in the log k values and none in T. The results (with 90% confidence limits) were:

$$E = 48{\cdot}29 \pm 0{\cdot}27 \text{ kcal. per mole}$$

$$\log_{10} A = 13{\cdot}47 \pm 0{\cdot}10; \qquad A = 3{\cdot}0 \times 10^{13} \text{ (sec.}^{-1}\text{)}$$

[The corresponding results for cyclohexyl chloride decomposition (total of 90 runs with and without inhibitor) were *

$$E = 49{\cdot}19 \pm 0{\cdot}52 \text{ kcal. per mole}$$

$$\log_{10} A = 13{\cdot}50 \pm 0{\cdot}18; \qquad A = 3{\cdot}2 \times 10^{13} \text{ (sec.}^{-1}\text{).]}$$

In order to check the effect of surface upon the rate of decomposition, ten runs were made in a reaction vessel packed with glass tubes and seasoned by the products of pyrolysis of allyl bromide. As shown in Table 5, a 14-fold increase in surface : volume ratio resulted in only a slight (~15%) increase in the rate, and decomposition in the unpacked vessel was therefore almost entirely homogeneous. (Runs in unpacked, unseasoned vessels were ~100-fold faster than those in seasoned vessels.)

TABLE 5. *Decompositions in a packed vessel.*

Temp.	309°	326°	342°	359°
Mean 10^5k_1 (sec.$^{-1}$)	2·69 (3 runs)	8·10 (2 runs)	22·6 (2 runs)	67·2 (3 runs)

The addition of small amounts of bromine to decomposing cyclopentyl chloride at 326° caused a slight but barely significant increase in the rate of pyrolysis (Table 6). Since bromine

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* This equation differs slightly from that previously reported [3] and now includes a " dead-space " correction.

[11] Maccoll and Thomas, *J.*, 1955, 2445.
[12] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
[13] Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053.
[14] Swinbourne, *J.*, 1960, 2371.

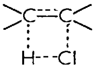
has been shown [15] to act as a stimulant for radical-chain reactions, it was concluded that these reactions were not readily sustained by the reacting mixture.

TABLE 6. *Effect of added bromine* (*at* 326°).

p_0 (cyclopentyl chloride) (mm.)	105	108	104
p (bromine) (mm.)	0	8	5
10^5k_1 (sec.$^{-1}$)	7·0	8·0	7·6

DISCUSSION

Cyclopentyl chloride has been shown to pyrolyse in " seasoned " reaction vessels by a nearly homogeneous first-order reaction to yield cyclopentene and hydrogen chloride. Side reactions are negligible. The absence of induction periods, the lack of inhibition by cyclohexene, and the relatively small effect of added bromine upon the rate provide evidence against a radical-chain mechanism for the pyrolysis. The magnitude of the activation energy (48·3 kcal./mole) eliminates the possibility of a radical non-chain process of the type discussed by Daniels and Veltman,[15] since the activation energy for such a mechanism must be of the order of the energy of homolysis of a secondary C–Cl bond [16] (∼82 kcal./mole). The results, however, are consistent with a unimolecular elimination of hydrogen chloride through a four-centre transition state (as inset) proposed by Barton and his co-workers.[17,18] The Arrhenius A factor, $3{\cdot}0 \times 10^{13}$ (sec.$^{-1}$) is of a magnitude regarded as " normal " for a unimolecular process, and the activation energy is slightly lower than for other secondary chlorides which have been studied.[3,18,19] The lower activation energy for the unimolecular decomposition of the cyclopentyl compound is also shown by the corresponding bromides [4,5,20] (see Table 7).



Although the bromides decompose about ten times as fast as the corresponding chlorides, both sets of compounds show similar rate sequences, as shown in Table 8 (the rate for the s-butyl compound has been taken as unity in each case). The close agreement between the two sets of data is indicative of a common mechanism. The cyclohexyl and s-butyl compounds pyrolyse at about the same rate, and both decompositions involve the elimination of a secondary hydrogen atom together with the secondary chlorine, while in the case of the isopropyl compound, a primary hydrogen atom is eliminated and the pyrolysis rate is correspondingly lower. Cyclopentyl chloride and bromide pyrolyse at approximately twice the rate of the corresponding cyclohexyl and s-butyl compounds, and an explanation for this abnormality can be provided in terms of the conformational characteristics of the five-membered ring: If the 4-centre transition state requires a planar arrangement of the halogen atom, the β-hydrogen atom, and the two carbon atoms

TABLE 7. *Unimolecular dehydrohalogenations in the gas phase.*

	Chlorides		Bromides	
	E (kcal./mole)	log A	E (kcal./mole)	log A
Isopropyl	50·5	13·4	47·8	13·62
s-Butyl	50·1	13·75	46·5	13·53
Cyclohexyl	49·2	13·50	46·1	13·38
Cyclopentyl	48·3	13·47	43·7	12·84

TABLE 8. *Relative rates of pyrolysis of chlorides and bromides* (367°).

	Isopropyl	<	s-Butyl	∼	Cyclohexyl	<	Cyclopentyl
RCl	0·3	:	1·0	:	1·1	:	2·1
RBr	0·4	:	1·0	:	1·0	:	1·9

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

[16] Lane, Linnett, and Oswin, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361.

[17] Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

[18] Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114.

[19] Stone, M.Sc. Thesis, London, 1958.

[20] Maccoll and Thomas, *J.*, 1955, 979; Kale, Maccoll, and Thomas, *J.*, 1958, 3016.

to which these are attached, then this situation is stereochemically favoured by the almost planar cyclopentane ring and not by cyclohexyl or straight-chain alkyl compounds in which the halogen and β-hydrogen atoms would be required to move from the more energetically favoured " staggered " position to one of " eclipse." The increased reactivity of cyclopentyl compounds may therefore be regarded as an example of " steric acceleration."

Analogous behaviour has been observed for the solvolysis of the corresponding toluene-*p*-sulphonates and arylsulphonates,[1] and a similar explanation has been proposed.[21] In both solution and the gas phase, the cyclohexyl compound has approximately the same reactivity as a secondary substituted straight-chain paraffin.

The enhanced rate of pyrolysis of cyclopentyl chloride may be attributed to a lower activation energy rather than to a variation in the *A* factor. The difference between the heats of hydrogenation of gaseous cyclopentene and cyclohexene is of the same order of magnitude (1·7 kcal./mole [22]) and it would be of interest to the present study to determine the corresponding enthalpy difference for the hydrohalogenation.

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

[22] Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831.