816. *The Kinetics of the Pyrolysis of* 1-*Chloropentane*

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1-Chloropentane decomposes in " seasoned " reaction vessels at 396—456° to hydrogen chloride and pent-1-ene by a nearly homogeneous first-order reaction. There is a slow subsequent isomerisation of pent-1-ene to pent-2-enes. For initial pressures of 1-chloropentane within the range 50—450 mm. the rate of decomposition is expressible as $k_1 = 10^{14.61}\exp(-58{,}300/\boldsymbol{R}T)$ sec.$^{-1}$. The results are similar to those previously reported for other primary chlorides and are consistent with a unimolecular mechanism for the elimination of hydrogen chloride.

THE compounds chloroethane, 1-chloropropane, and 1-chlorobutane are reported[1] to decompose in the gas phase by a mechanism involving direct unimolecular elimination of hydrogen chloride. The corresponding bromides (including also 1-bromopentane and 1-bromohexane) decompose by simultaneous chain and unimolecular mechanisms.[2] All these studies were carried out in " seasoned " Pyrex glass reaction vessels coated with carbonaceous films, and it was expected that, in such a vessel, dehydrochlorination of 1-chloropentane would proceed *via* a unimolecular mechanism.

EXPERIMENTAL

Descriptions of the apparatus and of the experimental methods have been given elsewhere.[3]

1-Chloropentane, prepared from 1-pentanol and thionyl chloride,[4] was distilled over concentrated sulphuric acid, washed in turn with sodium hydrogen carbonate solution and water, dried ($CaCl_2$), fractionally distilled, and collected at 108·1—108·2°/768 mm. It had n_D^{20} 1·4118 (lit.,[5] b. p. 106°/725 mm., n_D^{20} 1·4128). The purity of this and other reagents was checked by gas chromatography.

Reproducible behaviour for the pyrolysis of 1-chloropentane in the range 396—456° was obtained in Pyrex glass reaction vessels (~ 350 ml.), which had first been " seasoned " by decomposing allyl bromide at 520° in them. No fast starts or induction periods were observed but graphs of time (t) against log ($2p_0 - p$) showed deviation from straight lines after the first 20% increase in pressure (see Figure). Prolonged pyrolysis gave " final " pressures which were significantly greater than twice the initial pressures ($p_f/p_0 \sim 2{\cdot}4$). The extent of decomposition estimated from titration of the hydrogen chloride formed during the initial stages of the pyrolysis agreed closely with that predicted from pressure changes (Table 1).

TABLE 1

Decomposition from pressure change and hydrogen chloride analysis

Temp.	406·6°	406·8°	406·6°	406·9°	406·7°	406·9°	416·0°
p_0 (mm.)	210	201	199	175	271	243	203
Decomp. (%) (press.)	15·4	19·6	24·0	27·9	30·0	32·0	44·7
Decomp. (%) (anal.)	15·4	20·0	25·0	27·1	28·2	30·9	43·4

Gas-chromatographic analysis * disclosed pent-1-ene to be the main organic reaction product with smaller amounts of pent-2-enes, the relative proportion of the latter increasing in the later stages of the decomposition. For example, at 25% decomposition at 427°, the products were

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* Columns used were, (*i*) 20% w/w of Apiezon L grease on Celite at 60° (4 ft.), (*ii*) 20% w/w of Squalane on Celite at 22° (4 ft.), (*iii*) Squalane coated on 0·026 inch bore copper tube at 22° (200 ft.), (*iv*) alumina treated with 5% w/w silicone oil at 50° (3 ft.).

[1] D. H. R. Barton and K. E. Howlett, *J.*, 1949, 155; D. H. R. Barton, A. J. Head, and R. J. Williams, *J.*, 1951, 2039.

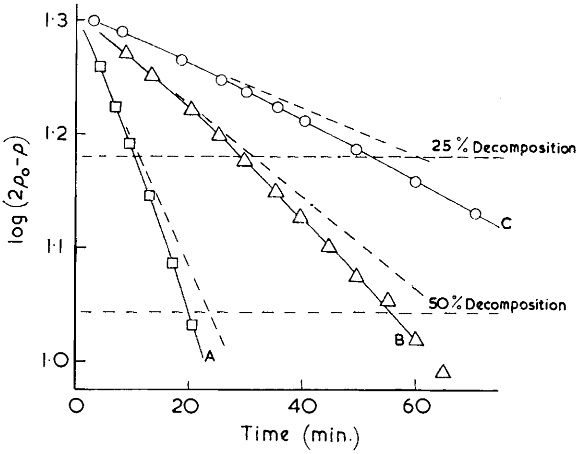
[2] A. E. Goldberg and F. Daniels, *J. Amer. Chem. Soc.*, 1957, **79**, 1314; A. Maccoll and P. J. Thomas, *J.*, 1957, 5033; P. J. Thomas, *J.*, 1959, 1192; J. H. S. Green, A. Maccoll, and P. J. Thomas, *J.*, 1960, 184.

[3] E. S. Swinbourne, *J.*, 1960, 4668; A. Maccoll and E. S. Swinbourne, *J.*, 1964, 149.

[4] A. I. Vogel, " Elementary Practical Organic Chemistry," Longmans, Green and Co., London, 1957, Part I, p. 167.

[5] F. C. Whitmore, F. A. Karnatz, and A. H. Popkin, *J. Amer. Chem. Soc.*, 1938, **60**, 2540.

as follows (mole %): pent-1-ene 96, pent-2-enes (*cis* and *trans*) ~1, other products (mainly propene with some n-butene and ethane) ~3. The equilibrium mixture of n-pentenes at the same temperature, as estimated from thermodynamic data,[6] is pent-1-ene 17%, *cis*-pent-2-ene 33%, *trans*-pent-2-ene 50%. Kinetic runs carried out in the presence of propene and in packed vessels gave no significant change in the pyrolysis products. A check on the stability of pent-1-ene at 442° in the presence of an equal quantity of hydrogen chloride showed that it isomerised to pent-2-ene (*cis* and *trans* mixture) at approximately one tenth the rate of 1-chloropentane decomposition. (The isomerisation in the absence of hydrogen chloride was about ten times slower again.) The isomerisation was accompanied by decomposition of the pentenes, the products of which [7] were identical with the minor products of 1-chloropentane pyrolysis.



First-order plots for pyrolysis of 1-chloropentane: (A) 434°, p_0 = 201 mm.; (B) 416°, p_0 = 202 mm.; (C) 407°, p_0 = 202 mm.

Rate Studies.—First-order rate coefficients, k_1 were estimated from the initial slopes of the graphs of log $(2p_0 - p)$ against t, the effect of "dead-space" (<1%) in the reaction system being ignored. Values of k_1, at a given temperature, showed no dependence upon the initial pressure of 1-chloropentane within the range 50—450 mm. Table 2 shows typical results for the decomposition at 436°, and the mean rate coefficients (with 90% confidence limits of the mean) at five temperatures are shown in Table 3.

TABLE 2

Decompositions at 436°

p_0 (mm.)	96	124	155	182	226	266	326	466
10^5k_1 (sec.$^{-1}$)	43·4	46·4	46·7	47·5	45·3	48·7	47·8	44·1

TABLE 3

The temperature dependence of rate coefficient

Temp.	398·4°	406·6°	426·6°	436·2°	456·0°
10^5k_1 (sec.$^{-1}$)	3·95 ± 0·37	8·56 ± 0·07	22·1 ± 0·7	46·3 ± 0·8	128 ± 4
No. of runs	7	6	12	15	7

The rate of decomposition was not greatly affected by the addition of propene (Table 4) and runs in a packed vessel, coated and seasoned as before but having a six-fold increase in surface to volume ratio, were about 30% faster than those in the unpacked vessel (Table 5).

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[6] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburg, 1953, p. 758.

[7] A. I. M. Keulemans and S. G. Perry in "Gas Chromatography, 1962," ed. van Swaay, Butterworths, London, 1962, p. 356.

TABLE 4

Effect of added propene (at 427°)

p_0(1-Chloropentane) (mm.)	150 *	51	102	146	184	204	220
p(Propene) (mm.)	0	245	116	108	111	109	10
10^5k_1 (sec.$^{-1}$)	22·8 *	19·0	21·8	22·3	21·2	20·8	23·0

* Mean values for six runs.

TABLE 5

Decompositions in a packed vessel

Temp.	403°	427°
Packed vessel, mean 10^5k_1 (sec.$^{-1}$)	7·9 (8 runs)	32·0 (14 runs)
Unpacked vessel, 10^5k_1 (sec.$^{-1}$) *	5·7	25·0

* Calc. from the Arrhenius equation.

From a total of 86 kinetic runs in the unpacked reaction vessel, the best straight line of log k_1 plotted against $1/T$ by the least-squares procedure gave the following values (with 90% confidence limits) for the constants in the Arrhenius equation, $k_1 = A \exp(-E/\mathbf{R}T)$:

$$E = 58{\cdot}32 \pm 1{\cdot}49 \text{ kcal./mole}^{-1}$$
$$\log_{10} A = 14{\cdot}61 \pm 0{\cdot}46;\ (A = 4{\cdot}1 \times 10^{14} \text{ sec.}^{-1}).$$

DISCUSSION

The decomposition of 1-chloropentane in seasoned reaction vessels at 396—456° is nearly homogeneous and of the first order, with hydrogen chloride and pent-1-ene as the main reaction products. Side-reactions are negligible in the early stages of the decomposition. There are no induction periods, and the addition of propene causes no appreciable change in the products or in the reaction velocity. These results are consistent with a unimolecular mechanism for the elimination of hydrogen chloride. Further evidence in support of this mechanism is provided by the agreement between the estimated values for the constants in the Arrhenius equation with those reported for other primary chlorides [1,8] (see Table 6). The slightly higher activation energy for the ethyl compound is also shown by the corresponding bromides [2] in which the radical-chain component of the decomposition has been maximally suppressed by the addition of propene or cyclohexene. It is also of interest to compare the relative rates for the pyrolysis of the chlorides at 420° with those of the bromides (radical-chain inhibited) at 381°, taking the rate for chloroethane as unity

TABLE 6

Unimolecular dehydrohalogenations in the gas phase

	Primary chlorides		Primary bromides	
	log A	E (kcal./mole)	log A	E (kcal./mole)
Ethane	14·60(13·51)	60·8(56·61)	13·42	53·9
Propane	13·45(13·50)	55·0(55·08)	12·90	50·7
Butane	14·0(13·63)	57·0(55·15)	13·18	50·9
Pentane	14·61(13·81)	58·3(55·33)	13·09	50·5
Hexane	—	—	13·13	50·5

The values [9] in parentheses are for the pyrolysis in silica vessels coated with potassium chloride

TABLE 7

Relative rates of pyrolysis of chlorides (420°) and bromides (381°)

	Ethane	Propane	Butane	Pentane	Hexane	Dodecane [10]
Primary chloride	1	3	4	6	—	12
Primary bromide	1	4	5	6	7	—

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[8] D. H. R. Barton and A. J. Head, *Trans. Faraday Soc.*, 1950, **46**, 123.

[9] H. Hartmann, H. G. Bosche, and H. Heydtmann, *Z. phys. Chem.* (*Frankfurt*), 1964, **42**, 329.

[10] F. Erbe, T. Grewer, and K. Wehage, *Angew. Chem.*, 1962, **74**, 988.

(Table 7). The close agreement between the data for the two sets of compounds is strongly indicative of a common mechanism.

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