

23. Gas Phase Eliminations. Part V.* The Kinetics of the Pyrolysis of Neopentyl Chloride.

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Gaseous neopentyl chloride decomposes in "seasoned" reaction vessels at 444° by the following four simultaneous reactions: (1) (75%) to hydrogen chloride and an equilibrium mixture of methylbutenes; (2) (10%) to methyl chloride and isobutene; (3) (7%) to methane and 1-chloro-2-methylpropene; (4) (7%) to methane and 3-chloro-2-methylpropene with subsequent rapid decomposition of the latter. The results are consistent with a view that reaction (1) is homogeneous and unimolecular, involving Wagner-Meerwein migration of a methyl group, with $10^5 k_1 \sim 2.8 \text{ sec.}^{-1}$, about one-quarter of the rate for dehydrochlorination of ethyl chloride. Reactions (2-4) are partly heterogeneous and are analogous to the pyrolysis of neopentane to methane and isobutene.

RECENT papers¹ have stressed analogies between gas-phase pyrolysis of halogenated hydrocarbons and the reactions of these and related compounds in polar solvents. A halogen-carbonium ion-pair transition state has been proposed for unimolecular dehydrohalogenation in the gas phase in preference to the earlier suggestion of a four-centre transition state² involving the halogen atom, a β -hydrogen atom, and the two carbon atoms to which these are bonded. Neopentyl chloride has no β -hydrogen atom, but in view of the above analogies and because the reaction of neopentyl compounds in solution frequently results in rearranged products,^{3,4} it was expected that dehydrochlorination of neopentyl chloride in the gas phase might be accompanied by Wagner-Meerwein rearrangement of the carbon skeleton with the formation of methylbutenes.

EXPERIMENTAL

Materials and Procedure.—Neopentyl chloride was prepared by the gas-phase photochlorination of neopentane: Chlorine and neopentane, from cylinders, were mixed in a water-cooled Pyrex glass-coil condenser which was irradiated with a 200-w tungsten lamp. A 100% excess of neopentane was used. (With an excess of chlorine a vigorous reaction resulted in a tar-like product.) Crude neopentyl chloride dropped into a receiving flask under the condenser, and the excess of neopentane was recovered by condensation in traps cooled with ice-salt. Recovered neopentane was recycled, after being washed with sodium hydroxide solution and dried over calcium chloride. The crude product was shaken in turn with sodium hydroxide solution, concentrated sulphuric acid, and saturated sodium hydrogen carbonate solution, dried (CaCl_2), fractionally distilled, and collected at 84.3-84.4°/752 mm. It had n_D^{20} 1.4045 (lit.,⁴ 84.4°/760 mm., n_D^{20} 1.4042) (Found: C, 56.2; H, 10.5; Cl, 33.8. Calc. for $\text{C}_5\text{H}_{11}\text{Cl}$: C, 56.4; H, 10.3; Cl, 33.3%). The yield of pure neopentyl chloride was ~20% (molar) on neopentane.

The decompositions were carried out in a Pyrex glass vessel (~420 ml.) housed in a heated metal-block thermostat. The apparatus and experimental methods have been described elsewhere.⁵ Fast starts were observed for runs carried out at 405° in vessels freshly "seasoned" with the pyrolysis products of allyl bromide. This behaviour was also noted for a number of alkyl chlorides by Barton, Head, and Williams, and by Howlett,⁶ who found that "normal" kinetic

* Part IV, *J.*, 1963, 5919.

¹ Maccoll and Thomas, *Nature*, 1955, **176**, 392; Maccoll in "Theoretical Organic Chemistry" (Kekulé Symposium), Butterworths, London, 1959, p. 230; Maccoll in "The Transition State," *Chem. Soc. Special Publ.* No. 16, 1962, p. 159.

² Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *ibid.*, 1950, **46**, 114.

³ Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274; Whitmore and Rothrock, *ibid.*, p. 3431; Whitmore, Whittle, and Popkin, *ibid.*, 1939, **61**, 1586; Dostrovsky and Hughes, *J.*, 1946, 164, 166, 171; Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.

⁴ Whitmore and Fleming, *J. Amer. Chem. Soc.*, 1933, **55**, 4161.

⁵ Swinbourne, *J.*, 1960, 4668.

⁶ Barton, Head, and Williams, *J.*, 1951, 2039; Howlett, *J.*, 1953, 945.

behaviour was obtained after further treatment of the chloride with sulphuric acid. Such treatment of neopentyl chloride, however, gave no significant improvement in kinetic behaviour. Runs carried out in the presence of propene and cyclohexene (commonly used as radical-chain inhibitors⁷) also gave fast starts with no apparent decrease in reaction rate. Below 50% decomposition, the products were identified as hydrogen chloride and methylbutenes, together with ~1% of methyl chloride, ~1% of isobutene, and ~3% of methane. The fast starts were attributed to a surface effect, and the vessels were therefore seasoned by two weeks' contact with decomposing neopentyl chloride at ~470° (~30 runs); during this time, the rates of successive runs (as measured by pressure increase) gradually fell, and eventually became consistent at about one-fifth of the value for a freshly coated vessel. The value of p_t/p_0 found was ~2.5 (significantly greater than 2.0). The kinetic runs did not show fast starts or induction periods, and graphs of time (t) against $\log(2p_0 - p)$ gave reasonable straight lines over the first 40% increase in pressure at 444° and the first 25% at 466°. The reaction was therefore studied in some detail at 444°.

Analysis of Products.—Even with rapid sampling of the reaction mixture by direct condensation of the contents of the reaction vessel into a phial cooled in liquid nitrogen, there was considerable combination of the methylbutenes with hydrogen chloride to form t-pentyl chloride. This greatly complicated the analytical procedures. For determination of hydrogen chloride the reaction mixture was condensed into a 500-ml. bulb containing 20 ml. of 3 : 7 ethanol-water cooled in liquid nitrogen. The bulb was sealed, heated to 60°, and allowed to cool overnight (this caused complete hydrolysis of tertiary chlorides with negligible hydrolysis of primary chlorides). The contents of the phial were then titrated with alkali. Other products were analysed by gas chromatography, the reaction mixture being collected in tap vessels from which samples were taken. Identification was by comparison with the retention times of standard samples on various stationary phases (*e.g.*, 25% w/w of ethyl acetoacetate on Celite at 20°, and 20% of w/w silicone oil on Celite at 55°), and, in the case of 1-chloro-2-methylpropene, by fraction-cutting combined with infrared spectroscopy. The addition of a slight excess of ammonia to the mixture in the reactor immediately before sampling, considerably reduced the reaction between the methylbutenes and hydrogen chloride, but difficulty was still experienced in obtaining reproducible analyses for methylbutene (these analyses were probably low). Methane and hydrogen had identical retention times on the columns used, and therefore analysis for each was carried out separately, first with hydrogen and then with methane as carrier gas. Samples were taken over the range of initial pressures of neopentyl chloride 20–40 cm., and over the range of decomposition 10–40%. Table 1 shows the products found for samples within the decomposition range 10–30%; over this range, analyses disclosed no major variation in the nature or proportion of the products, but beyond 30% decomposition there was a significant increase in the proportion of methane, and small amounts of other unidentified products were detected.

TABLE 1.

Products from neopentyl chloride decomposed at 444° (10–30% decomposition range).

Hydrogen chloride	0.85 mole/mole	1-Chloro-2-methylpropene	0.07 mole/mole
Methylbutenes (equil. mixture)...	0.70 "	Methane	0.25 "
Methyl chloride	0.10 "	Hydrogen	0.01 "
Isobutene	0.11 "		

The stability of the methylbutenes in the presence of an equimolar quantity of hydrogen chloride was tested in a seasoned reaction vessel at 444°; it was concluded that, in the present study, secondary decomposition of methylbutenes was of minor importance only. Rearrangement to an equilibrium mixture was very rapid (this agrees with observations by Stimson and Watson⁸); analysis of freshly trapped samples gave 2-methylbut-2-ene : 2-methylbut-1-ene : 3-methylbut-1-ene = 65 : 30 : 5, but deviations from this analysis were observed for samples stored for several days at room temperature.

Kinetic Results.—The rate coefficient (k_1) for the overall decomposition of neopentyl chloride was estimated from the slope of the graph of $\log [p_0/(2p_0 - p)]$ against t (see Figure), corrections being applied for 2% of "dead-space" in the reaction system,⁹ and for the formation of slightly

⁷ Barton and Howlett, *J.*, 1949, 155; Maccoll and Thomas, *J.*, 1955, 2445.

⁸ Stimson and Watson, *J.*, 1961, 1392.

⁹ Allen, *J. Amer. Chem. Soc.*, 1934, 56, 2053.

more than one mole of product per mole of neopentyl chloride decomposed. Table 2 lists values for k_1 at 444°. The results had more scatter than usual for studies of this kind, but there

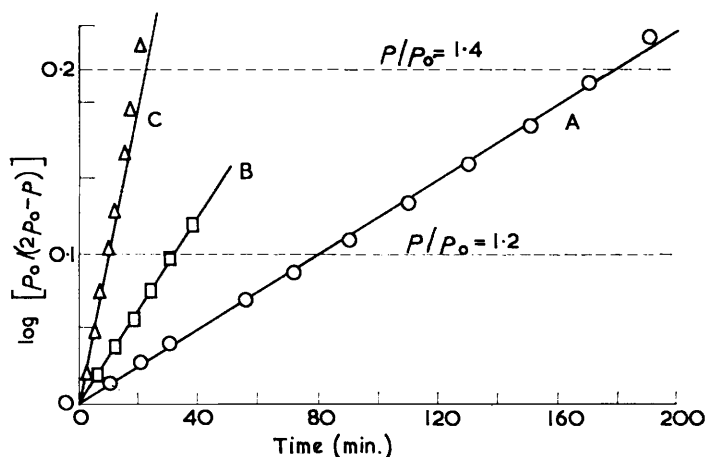
TABLE 2.
Decompositions at 444°.

p_0 (mm.)	95	196	220	227	231	244	246	290
$10^5 k_1$ (sec. ⁻¹)	2.9	3.1	4.1	4.2	4.2	3.8	3.3	3.8
p_0 (mm.)	310	338	345	362	362	364	163 *	228 †
$10^5 k_1$ (sec. ⁻¹)	4.4	3.2	4.1	3.9	4.2	4.2	2.9	4.2

*† Decomposition in the presence of * 197 and † 50 mm. of propene.

was no obvious variation of k_1 with changes in the initial pressure of neopentyl chloride, and the rate of decomposition was not greatly affected by the addition of propene. For all runs in Table 2, the mean value of $10^5 k_1 = 3.8 \text{ sec.}^{-1}$

In order to check the effect of surface upon the decomposition, runs were made in a packed vessel coated and seasoned as before, but having a six-fold increase in surface-volume ratio.



First-order plots for pyrolysis of neopentyl chloride ($p_0 \sim 200$ mm.) at (A) 444°, (B) 466°, and (C) 486°.

Table 3 shows the products formed during the early stages of pyrolysis of neopentyl chloride in this vessel. Values of k_1 for the overall decomposition of neopentyl chloride in the packed reactor at 444° are shown in Table 4.

The absence of 3-chloro-2-methylpropene from the products (Table 1) suggested the possibility of the formation and subsequent rapid decomposition of this compound under the reaction conditions. This could also account for the high proportion of methane and for the

TABLE 3.

Products in a packed vessel at 444° (per mole of neopentyl chloride decomposed).

Hydrogen chloride	0.76 mole/mole	1-Chloro-2-methylpropene	0.11 mole/mole
Methylbutenes	0.60 ,,	Methane	0.34 ,,
Methyl chloride	0.15 ,,	Hydrogen	0.02 ,,
Isobutene	0.18 ,,		

TABLE 4.

Decompositions in a packed vessel (444°).

p_0 (mm.)	96	96	158	216	310	320	334	346	385	407	442
$10^5 k_1$ (sec. ⁻¹) ...	4.0	2.9	3.2	3.8	4.3	3.1	3.6	4.5	3.2	4.1	3.7

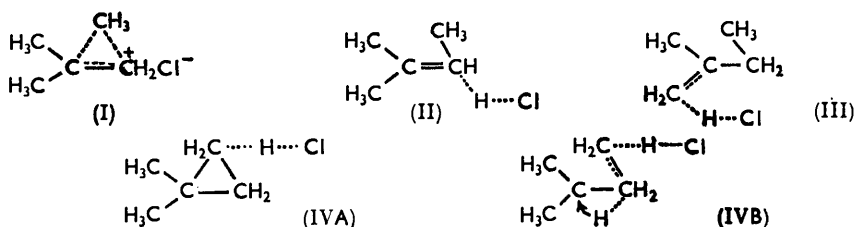
Mean $10^5 k_1 = 3.7 \text{ sec.}^{-1}$.

stoichiometric excess of hydrogen chloride over the methylbutenes. A check on the stability of 3-chloro-2-methylpropene in a coated vessel at 444° showed that it decomposed at ~12 times the rate of neopentyl chloride, to form hydrogen chloride and methane as the main gaseous products (approximately one mole of each per mole of compound decomposed).

DISCUSSION

The product analysis in Table 1 can be interpreted in terms of the decomposition of neopentyl chloride proceeding by four simultaneous reactions: *Reaction 1* (75%), formation of hydrogen chloride and an equilibrium mixture of methylbutenes. *Reaction 2* (10%), formation of methyl chloride and isobutene. *Reaction 3* (7%), formation of methane and 1-chloro-2-methylpropene. *Reaction 4* (7%), formation of methane and 3-chloro-2-methylpropene, with subsequent rapid decomposition of the latter to an equimolar mixture of methane and hydrogen chloride as gaseous products. This scheme predicts the following products (moles per mole of neopentyl chloride decomposed): HCl 0.82, methylbutenes 0.75, methyl chloride 0.10, isobutene 0.10, 1-chloro-2-methylpropene 0.07, methane 0.21. (In the packed vessel, *reaction 1* accounts for ~65% of the total neopentyl chloride decomposed.)

The kinetic data are consistent with the view that reaction 1 is of the first order and homogeneous: at 444°, $10^5 k_1 = 2.8 \text{ sec.}^{-1}$ (unpacked vessel), 2.4 sec.^{-1} (packed vessel); after allowance for the scatter of results there is no significant difference between these values. The absence of induction periods and the insignificant effect of added propene upon the rate are further evidence in support of the view that this reaction is unimolecular. It is difficult to propose a reasonable scheme which accounts for the formation of large quantities of methylbutenes from neopentyl chloride by a radical process. In view of the nature of the products, unimolecular dehydrochlorination of neopentyl chloride in the gas phase must be accompanied by a Wagner-Meerwein rearrangement of the carbon skeleton. Since the first Note about this work,¹⁰ similar rearrangements have also been reported for the gas-phase pyrolysis of neopentyl chloroformate,¹¹ bornyl chloride,¹² and isobornyl chloride,¹³ confirming the importance of quasi-heterolytic mechanisms for many gas-phase reactions. In the case of neopentyl chloride, a transition state (I) may be envisaged, resulting from a critical elongation and polarisation of the carbon-chlorine



bond, followed or accompanied by a methyl migration from the β - to the α -position, as illustrated. Proton removal from the original α -position (II) by the chloride ion would result in the formation of 2-methylbut-2-ene; 2-methylbut-1-ene would be formed by proton removal from the original γ -position (III). Proton removal from the migrating methyl group could result in the formation of 1,1-dimethylcyclopropane* (IVA), almost certainly

* Small quantities of this compound are formed¹⁴ during the decomposition of neopentyl alcohol on alumina at 345°.

¹⁰ Maccoll and Swinbourne, *Proc. Chem. Soc.*, 1960, 409.

¹¹ Lewis and Herndon, *J. Amer. Chem. Soc.*, 1961, **83**, 1901.

¹² Bicknell and Maccoll, *Chem. and Ind.*, 1961, 1912.

¹³ Bicknell, personal communication.

¹⁴ Pines, *J. Amer. Chem. Soc.*, 1961, **83**, 3274.

unstable¹⁵ in the presence of hydrogen chloride at 444°, or in the formation of 3-methylbut-1-ene by subsequent migration of a hydrogen atom from the original α - to the β -position (IVB). Because of rapid rearrangement among the methylbutenes, the present study unfortunately does not reveal the compound(s) primarily formed in the dehydrochlorination.

TABLE 5.

Relative rates of elimination of hydrogen chloride from primary chlorides.

	Ethyl	Propyl	Isobutyl	Neopentyl
In gas phase (444°)	1	3	4	0.2
On Pyrex glass (413°)	1	5	12	20

Table 5 shows that in the gas phase, dehydrochlorination of neopentyl chloride is slower than for other primary chlorides^{16,17} (the rate for ethyl chloride has been taken as unity). Comparison with solution reactions also shows that neopentyl bromide undergoes solvolysis more slowly than ethyl bromide in wet formic acid at 95° (relative rates 1 : 2);¹⁸ however, for the heterogeneous dehydrochlorination on the surface of Pyrex glass, the rates show a steady increase from ethyl to neopentyl chloride with each successive substitution of a β -methyl group.¹⁷

Reactions 2—4, which account for ~24% of the overall decomposition of neopentyl chloride in the unpacked vessel are probably partly heterogeneous, in view of the increase in the products from these reactions in the packed vessel. These reactions may be compared with the pyrolysis of neopentane to methane and isobutene for which Engel, Combe, Letort, and Niclause¹⁹ reported an order of 1.5 in the initial stages of decomposition between 500° and 570°, the rate coefficient being expressed as $k_{1.5} = 1.5 \times 10^{13} \exp(-51,500/RT)$ sec.⁻¹ mole^{-0.5} c.c.^{0.5}. Extrapolating from this equation to 444° and expressing k as a first-order coefficient for 250 mm. of reactant (average for the present study), we obtain $10^6 k_1 = 7$ sec.⁻¹. This compares closely with reactions 2 + 3 + 4 (above) for which $10^6 k_1 = 9$ sec.⁻¹. According to Peard, Stubbs, and Hinshelwood,²⁰ the nitric oxide-inhibited pyrolysis of neopentane is of the first order, and their data extrapolated to 444° give $10^6 k_1 = 3$ sec.⁻¹. Reactions 2—4 probably proceed by a mixture of radical, unimolecular, and heterogeneous mechanisms.

More information on the mechanism of pyrolysis of neopentyl chloride should emerge from a study of this reaction over a range of temperatures and over a wider range of pressures, and from investigations of the pyrolysis of 1- and 3-chloro-2-methylpropene.

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¹⁵ Ross and Stimson, *J.*, 1962, 1602.

¹⁶ Barton and Howlett, *J.*, 1949, 165; Barton, Head, and Williams, ref. 6; Howlett, *J.*, 1952, 4487.

¹⁷ Shapiro, personal communication.

¹⁸ Dostrovsky and Hughes, ref. 3.

¹⁹ Engel, Combe, Letort, and Niclause, *Compt. rend.*, 1957, **244**, 453.

²⁰ Peard, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1952, *A*, **214**, 330.