

The Pyrolysis of Chloroalkenes. Part I. Allyl Chloride.

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Gaseous allyl chloride decomposes in the temperature range 370—475° by simultaneous non-chain, chain, and heterogeneous processes to yield, initially, allene and hydrogen chloride. The allene polymerises rapidly at these temperatures. By fractional distillation of the liquid reaction products some of the lower polymers have been identified. The pyrolysis of allyl chloride is the first dehydrochlorination which has been observed to be markedly heterogeneous under these experimental conditions.

In recent years the kinetics of the thermal decompositions of numerous chloroalkanes have been described (Barton, Head, and Williams, *J.*, 1952, 453; Howlett, *ibid.*, p. 3695; and references there cited). One general conclusion reached from these investigations is that a polychlorohydrocarbon decomposes, losing 1 mol. of hydrogen chloride and yielding a chloroalkene, much more rapidly than any subsequent reactions of these initial products. Thus, for the purpose of calculating rate constants, it has been assumed that the whole of the measured reaction refers to this first dehydrochlorination process. It is obviously desirable to check this by direct observation of the kinetics of decomposition of the pure chloroalkenes. No such physicochemical study has yet been reported. Allyl chloride was chosen as a representative unsaturated chloride. It was also hoped that suitable experimental conditions might be found for the production of allene or of methylacetylene, starting from allyl chloride.

EXPERIMENTAL

Apparatus and Materials.—The static apparatus employed for the kinetic work was essentially similar to that described by Barton and Howlett (*J.*, 1949, 155), and the results therefore refer to decomposition in vessels whose walls were covered with a coherent carbonaceous film.

In order to obtain the reaction products in quantity, dynamic experiments have also been performed. "Oxygen-free" nitrogen was purified over red-hot copper and passed through an oil flow-meter. It was then bubbled through an allyl chloride trap which could be kept at any desired temperature or by-passed if necessary. The gases passed through a 45-c.c. Pyrex tube reaction vessel of surface/volume ratio *ca.* 6 cm.⁻¹, in a manually operated, aluminium block, electric furnace. The reaction products were collected by passage through suitable traps and absorbents [*e.g.*, a 10° trap surmounted by a condenser; 2 water traps; 1 trap containing Ilosvay's reagent (cf. *Ber.*, 1899, 32, 2698); magnesium-barium perchlorate; a trap kept at

–80°, and finally concentrated sulphuric acid, for the successive removal of a thin tar, hydrogen chloride, acetylenes, (water), unchanged allyl chloride, and finally olefins]. The temperature of the furnace was measured with a base-metal thermocouple calibrated immediately before use. The walls of the reaction vessels were covered with a carbonaceous film before the collection of products was attempted.

Allyl chloride was prepared from allyl alcohol (cf. Vogel, "Textbook of Practical Organic Chemistry," p. 276). The purified product was redistilled immediately before its admission to the reservoir trap attached to the apparatus; it had b. p. 45.2° (corr.), n_D^{25} 1.4137. It was rapidly degassed and, when not being volatilised into the reaction vessel, was kept in the dark at –80° in order to retard polymerisation (Staudinger and Fleitmann, *Annalen*, 1930, 480, 92).

Results.—Maccoll (*J. Chem. Phys.*, 1949, 17, 1350) reported that, under experimental conditions similar to ours, allyl bromide eliminates hydrogen bromide in the range 320–380°. Pressure increases in a constant-volume system were approximately 50% when the dehydrobromination approached completion. This is consistent with the formation of hydrogen bromide and a dimer of allene.

The kinetics of the decomposition of allyl chloride have been studied in the range 370–475°. The course of this reaction could not be followed by pressure changes, for these were complex. The products of reaction were therefore analysed for hydrogen chloride by condensation in a 5-c.c. liquid-air trap connected to the reaction vessel, and subsequent titration. When the vessel was opened to this trap after a "kinetic" run the pressure fell to 0.1–0.5 mm. It is thus clear that other cracking reactions producing hydrogen or methane cannot occur to any appreciable extent. After a number of overnight runs in which the decomposition was allowed to approach completion at about 450°, the final pressure was 1.6–1.7 times that initially admitted. The incompleteness of condensation after these long-term experiments suggests that slight cracking of the reaction products, subsequent to, and not simultaneous with the main process, had occurred after 15 hr. at 450°. In both long- and short-term runs, hydrogen chloride determinations invariably indicated greater extents of decomposition than did the pressure changes (in the latter calculation it was assumed that 1 mol. of reactant gave 2 mols. of product), and there was no constant ratio between these two apparent extents of reaction. The reported results are based upon the analyses and therefore refer to the dehydrochlorination of allyl chloride. Determinations of hydrogen chloride from the 15-hr. runs (necessarily rough and low on account of the 2–3 mm. residual pressure) indicated an average of *ca.* 90% decomposition in this sense.

The dehydrochlorination of allyl chloride follows a first-order law to at least 30% decomposition over the initial pressure range 10–100 mm., as shown in Table 1, where velocity constants at 458° are given for different initial concentrations of reactant. There is clearly no significant variation of velocity constant.

TABLE 1.

| | | | | | |
|--------------------------------------|------|------|------|------|------|
| p_0 (mm.) | 11 | 16 | 32 | 48 | 70 |
| No. of runs | 27 | 20 | 31 | 15 | 19 |
| 10^5k (sec. ⁻¹) (mean) | 23.6 | 25.0 | 26.2 | 24.4 | 26.2 |

The mean velocity constants obtained at different temperatures are shown in Table 2 and may be summarised by the method of least squares, giving equal statistical weight to each experiment, as $k = 10^{9.10}e^{-42,500/RT}$ sec.⁻¹, for the rate constant of dehydrochlorination of allyl chloride in reaction vessels with product-fouled walls and of surface/volume ratio 2 cm.⁻¹. The reaction has also been studied in a packed vessel of surface/volume ratio 22 cm.⁻¹. These results are included (*p*) in Table 2. These velocity constants are 2–3 times those found in the unpacked vessel. The apparent activation energy of the overall reaction in the packed vessel (32 kcal./mole) is definitely lower than that in the "empty" vessel.

TABLE 2

| Temp. | No. of runs | 10^5k (sec. ⁻¹) (mean) | Temp. | No. of runs | 10^5k (sec. ⁻¹) (mean) | Temp. | No. of runs | 10^5k (sec. ⁻¹) (mean) |
|--------------|-------------|--------------------------------------|---------------|-------------|--------------------------------------|--------------|-------------|--------------------------------------|
| 475° | 22 | 41.1 | 440° <i>p</i> | 19 | 23.5 | 393° | 7 | 1.26 |
| 469 | 23 | 36.1 | 421 <i>p</i> | 8 | 14.2 | 380 | 6 | 1.07 |
| 458 | 112 | 25.2 | 420 | 12 | 4.80 | 378 <i>p</i> | 7 | 2.54 |
| 457 <i>p</i> | 17 | 40.3 | 397 <i>p</i> | 7 | 5.91 | 370 | 7 | 0.418 |
| 440 | 17 | 10.6 | | | | | | |

p = Packed reaction vessel.

Propylene is well established as a powerful inhibitor for the radical-chain decompositions of chlorohydrocarbons (Barton and Howlett, *J.*, 1951, 2033). Its effect upon the pyrolysis of allyl chloride has been studied in both packed and unpacked reaction vessels. A small decrease in velocity constant was observed on addition of propylene. Maximum inhibition was achieved with quite small amounts of this gas as is shown in Table 3, which gives some results obtained at

TABLE 3

| | | | | | | |
|-------------------------------------|------|------|------|------|------|------|
| p_0, C_3H_6 (mm.) | 0 | 1.2 | 1.9 | 10.8 | 11.9 | 17.9 |
| 10^5k (sec. ⁻¹) | 25.2 | 20.0 | 17.5 | 19.1 | 22.3 | 18.2 |

458° with 33 mm. initial pressure of allyl chloride. For the later inhibited experiments, the propylene pressure was therefore kept between 5 and 10 mm. The first-order velocity constants found under these conditions were independent of the allyl chloride concentration and are given in Table 4.

TABLE 4

| | | | | |
|--|------|---------------|------|---------------|
| Temp. | 420° | 420° <i>p</i> | 458° | 458° <i>p</i> |
| No. of runs | 6 | 14 | 30 | 29 |
| 10^5k (sec. ⁻¹) mean | 4.49 | 10.4 | 20.6 | 33.8 |

In a typical experiment for the collection and identification of the reaction products, nitrogen was passed through the flow apparatus at 4 c.c./min. (measured at 20°) for 175 hr., the furnace temperature being 505° ± 5°. During this time 104.2 g. of allyl chloride were volatilised and passed through the furnace with a hot contact time of 142 sec. The gas mixture entering the furnace contained about 40% of reactant, and hydrogen chloride titration showed that of the 1.36 moles passed through the furnace, 0.611 mole was decomposed. This corresponds to a velocity constant of 4×10^{-3} sec.⁻¹, *i.e.*, within a factor of 2 of that expected by extrapolation from the static results. This confirms that the same reaction as that measured kinetically is occurring in the dynamic runs. The total acetylenes were determined by Willstätter and Maschmann's modification of Ilosvay's test (*Ber.*, 1920, 53, 939). About 2% of acetylenes were found, based upon the allyl chloride consumed. Allene, estimated by distilling the diluted sulphuric acid trap liquor into sodium hypiodite and weighing the precipitated iodoform, averaged about 1% of the decomposed allyl chloride. Furthermore, the almost negligible increase in weight of the sulphuric acid trap indicated that the total olefins were of the same order as the allene. The main carbon balance was accounted for by the thin tar condensed at 10° immediately on leaving the furnace. The weight of this fraction was *ca.* 70% of the total possible allene formed. The remaining carbon was probably deposited as the carbonaceous layer in the furnace and exit tube, since deposition here was noticeably heavy. Fractional distillation of 10 g. of the tar gave a small amount boiling at *ca.* 50°, identified as allyl chloride, and then the following fractions which all showed unsaturation to bromine in carbon tetrachloride and were practically free from chlorine.

| Boiling range | Wt., g. | Odour | n_D^{20} | <i>M</i> |
|---------------|---------|--------------|------------|----------|
| 61—68° | 0.5 | Sharp | 1.4545 | 81 |
| 35—50/9 mm. | 0.8 | Turpentine | 1.5122 | — |
| 50—70/9 mm. | 0.4 | Turpentine | — | — |
| 71—80/9 mm. | 0.4 | Camphor | 1.5478 | — |
| 80—105/9 mm. | 0.7 | Paraffin | 1.5704 | 153 |
| Residue | 6.0 | Burnt rubber | — | — |

DISCUSSION

The tar fractionation products are almost identical in every respect with those obtained by Meinert and Hurd (*J. Amer. Chem. Soc.*, 1930, 52, 4540) and Lebedev (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1249) from the pyrolysis of allene. In particular, the fractions of *M* 81 and 153 correspond to Lebedev's reported dimer and tetramer of allene. Meinert and Hurd also found mainly liquid polymers with less than 10% of gaseous products under experimental conditions similar to ours. It seems, therefore, that, in the main, the pyrolysis of allyl chloride leads initially to allene and hydrogen chloride. The method is, however, quite unsuitable for producing allene or its isomers because allene polymerises at these temperatures faster than allyl chloride decomposes.

The decomposition of allyl chloride is the first gaseous dehydrochlorination which has

been observed to have an appreciable heterogeneous component even when reaction is conducted over a heavy carbonaceous surface. After correction of the observed velocity constants to zero surface/volume ratio, the homogeneous rate constant is found to be $k \approx 10^{10.1} e^{-46,000/RT}$ sec.⁻¹, whence the activation energy of the heterogeneous reaction is ca. 25 kcal./mole. This is definitely higher than that for the glass-catalysed heterogeneous pyrolysis of *tert.*-butyl chloride (Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725). Over our temperature range the homogeneous reaction is predominant but, if rate measurements could be carried out at lower temperatures, the heterogeneous reaction would be important and a pronounced curve would be apparent in the Arrhenius plot.

The effect of propylene upon the reaction shows that it is mainly non-chain in character, but that in the unpacked reaction vessel about 10% of the total is of the radical-chain type. This radical reaction is shown to be homogeneous by comparing the results in packed and in unpacked reaction vessels in the presence of inhibitor. If all the observed heterogeneity were due to chain reaction, the maximally inhibited reaction rate constant would be independent of the surface/volume ratio. This is not found experimentally. Therefore, the heterogeneous reaction is at least partly non-chain in character. Also, the difference between the velocity constants for the inhibited and the uninhibited reaction, *i.e.*, the rate constant for the chain process, is the same in both reaction vessels, showing that the chain reaction is homogeneous and also that the heterogeneous reaction is entirely non-chain in character.

It seems likely that the low efficiency of both the homogeneous processes is the reason for the marked heterogeneity of the total reaction. Maccoll (*loc. cit.*) considered allyl bromide to decompose by splitting of a C-Br bond—a conclusion borne out by the activation energy. A different mechanism is obviously involved in the present case, for the activation energy which we find is similar to that found by Maccoll, in spite of the higher C-Hal bond energy in allyl chloride.

It is interesting to compare the rate of decomposition of allyl chloride with that for 1 : 2-dichloropropane (Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114) because allyl chloride is probably amongst the monochloropropenes produced from the latter. In the temperature range investigated by Barton and Head the velocity constant for decomposition of allyl chloride averages about 13% of that for 1 : 2-dichloropropane. Thus if the velocity constants for the latter were computed for a 50% increase in pressure (which is probably a maximum), the error in assuming this to arise solely from the first reaction is less than 3%, which is not serious. In a series of 15-hr. runs, carried out above 700° K, Barton and Head's ratios of final to initial pressure (*ca.* 2.6) are just what would be expected from our results on the pyrolysis of allyl chloride.