THE PYROLYSIS OF CHLOROBENZENE

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A study of the thermal decomposition of chlorobenzene shows that two quite distinct mechanisms can operate according to the temperature. Between 770 and 800° C, the main products are hydrogen chloride, hydrogen and p:p'-dichlorodiphenyl; chlorine atoms and chlorophenyl radicals appear to be the principal carriers involved in a chain cycle in which there is little or no rupture of the aromatic ring. At higher temperatures (800-850° C), extensive ring-breaking occurs and quite large yields of vinyl chloride are obtained; here, a chain reaction is postulated in which C₂HCl fragments are important intermediate species. The occurrence of two competing mechanisms results in a well-defined negative temperature coefficient of reaction rate between 830 and 850° C; for on account of the increasing thermal instability of C₂HCl fragments the ring-breaking mechanism cases to operate and there is a consequent decrease in the rate of consumption of chlorobenzene by this process. At still higher temperatures, therefore, hydrogen chloride, hydrogen and p:p'-dichlorodiphenyl again become the main products.

Pyrolysis of chlorobenzene in the presence of added hydrogen yields products qualitatively similar to those obtained in its absence. The accelerating effect of hydrogen is most marked at temperatures where the ring-stripping mechanism is predominant. It is suggested that hydrogen favours the latter process by preventing recombination of chlorine atoms at the walls, while it hinders the ring-breaking reaction by stabilizing intermediate C_2HCl fragments.

In a recent investigation of the thermal decomposition of chlorobenzene,¹ it was shown that the main gaseous products are hydrogen chloride and hydrogen. No gaseous carbon compounds were found, nearly all the carbon apparently being deposited on the walls as a hard shiny film. Kinetically the reaction is composite, being partly a radical chain reaction, inhibited by nitric oxide and ammonia, and partly a process unaffected by these inhibitors. The fully inhibited reaction is homogeneous and is of the first order at high pressures but of the second order at lower pressures; it is probably a unimolecular decomposition of the aromatic compound. The chain reaction appears to involve a cycle in which chlorine atoms and chlorophenyl radicals are the chain carriers, and in which the chains are fairly short.

The absence of appreciable amounts of gaseous carbon-containing products in the decomposition of chlorobenzene and of the dichlorobenzenes² suggests that reaction consists essentially in the "stripping" of aromatic rings, and that the rings themselves remain largely intact during the breakdown process. Spectroscopic evidence³ indicates that the decomposition of aromatic radicals frequently results in the formation of polynuclear compounds, and small quantities of diphenyl and chlorodiphenyls have indeed been reported among the breakdown products of chlorobenzene.⁴ These findings confirm that reaction involves principally the fission of C—H or C—Cl bonds rather than the rupture of the aromatic ring.

The pyrolysis of chlorobenzene, which was previously studied in a static system,¹ has now been reinvestigated in a flow system. In this way, not only can considerably larger quantities of products be obtained, but by the use of short contact times, the products and unchanged reactants can be rapidly removed from the reaction zone, thus favouring the isolation and detection of labile intermediate

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compounds. It was thus hoped to obtain reliable analytical information about the course of the thermal decomposition of chlorobenzene over a wide range of experimental conditions.

EXPERIMENTAL

APPARATUS

The apparatus is shown diagrammatically in fig. 1. The reaction vessel A was made of transparent silica and had a volume of *ca*. 200 ml. The bulb B was used to store liquid chlorobenzene. It was attached to a reservoir R of *ca*. 500 ml capacity which, during a run, contained a "buffer" of reactant vapour which served to minimize changes in pressure. From R, the reactant vapour passed through the capillary leak L_1 into the reaction vessel. Pressures were measured on a capillary mercury manometer attached at M; a trap, packed with gold leaf, was placed between the mercury column and the rest of the system and prevented diffusion of mercury vapour into the apparatus.



FIG. 1.

Products and unchanged reactant emerging from the reaction vessel passed through the "cascade" of traps (T_2-T_6) to remove condensable materials. Non-condensable gases entered the combustion furnace C containing "wire-form" copper oxide. Here hydrogen and methane were oxidized to steam and carbon dioxide, which were condensed in T₇. Finally, between this trap and the pumping system, was interposed a second capillary leak L₂.

The electric furnace surrounding A was wound in three independently controlled sections to give a uniform temperature distribution over the length of the reaction vessel.⁵ The temperatures of this furnace and of that surrounding C were measured with chromelalumel thermocouples, which were regularly calibrated against a platinum-rhodium thermocouple. B was normally maintained between 45 and 60° C, the temperature being constant for any given run. R was heated to 95° C to ensure that only vapour passed from it into the rest of the system. All glass tubing in contact with readily condensable vapours was heated electrically to about 100° C to prevent condensation.

PURIFICATION OF REACTANTS

CHLOROBENZENE.—Chlorobenzene was purified by conventional methods and a sample was then distilled directly into B. Immediately before each run, the contents were thoroughly "out-gassed" by repeated melting and freezing under vacuum.

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HYDROGEN.—Cylinder hydrogen was passed over magnesium perchlorate and then over Hopcalite at 120° C; the resulting carbon dioxide was absorbed by Sofnolite. Oxygen was removed by passage over palladized asbestos at 350° C and any water formed was again absorbed by magnesium perchlorate. The purified hydrogen passed into the reaction system at H (fig. 1) via a needle-type reducing valve.

ANALYTICAL PROCEDURE

The quantity of chlorobenzene passing through the reaction vessel during a run was determined from the loss in weight of B. If, during a run, a blockage occurred in the exit tube of the reaction vessel, the reactant remaining in R could be condensed out in T_1 and analyzed, so that kinetic data could still be deduced from the run in question.

The unchanged chlorobenzene and its decomposition products emerging from the reaction vessel were separated by fractional condensation. Traps T_2 - T_4 were cooled in solid carbon dioxide and thus removed unchanged reactant and all readily condensable products, in addition to any carbonaceous "dust" carried over in the gas stream. Hydrogen chloride was condensed out in T_5 and T_6 which were surrounded by liquid nitrogen. Hydrogen and methane passed through C and the resulting water and carbon dioxide were collected in T_7 which was cooled in liquid nitrogen. Control experiments showed that, with the contact times used in this work, conversion to water and carbon dioxide was complete if the copper oxide was maintained at 530° C.

The contents of the various traps were analysed as follows.

Chlorobenzene.—n-Hexane was run into traps T_2 - T_4 . Since chlorobenzene was always present in large excess of other chlorine-containing compounds, the amount of unchanged reactant was determined by estimation of the total chlorine content of the solution. All the organically-bound chlorine was converted to chloride ions by treatment with sodium and *iso* propyl alcohol.⁶ The chloride concentration in the resulting solution was determined by Volhard's method.

Hydrogen chloride.—The contents of T_5 and T_6 were dissolved in aqueous ethanol, immediately after removal of the surrounding liquid nitrogen. The amount of hydrogen chloride in the resulting solution was determined either by Volhard's method or by titration with standard alkali; the two methods always gave results in excellent agreement.

Hydrogen.—The hydrogen was oxidized to steam in C and the water formed was collected in T_7 . The contents of T_7 were dissolved in anhydrous acetone and the water content of the resulting solution was found by allowing a measured volume to react with acetyl chloride and pyridine and then back-titrating the acetic acid formed with standard alkali.⁷

Methane.—Methane was oxidized to carbon dioxide which was condensed in T_7 together with any water formed. The CO₂-content of the acetone solution in this trap was found by direct titration of a known volume of this solution with standard alkali, phenolphthalein being used as indicator.

Other products.—Elementary carbon and readily condensable carbon-containing products were collected together with unchanged chlorobenzene in T_2 - T_4 . The solution was filtered and, after removal of a known volume of the filtrate for the determination of chlorobenzene, the remaining solution was distilled to remove hexane and residual chlorobenzene; the resulting viscous brown tar was placed in a vacuum desiccator for 24 h.

This tar contained a considerable proportion of the combined carbon and its constitution was investigated by elution chromatography.⁸ With alumina as absorbent and mixtures of petroleum ether and diethyl ether as eluents, it was possible to isolate certain fractions, the compositions of which were subsequently determined. The only pure compound isolated was p: p'-dichlorodiphenyl, the quantity of which was determined by direct weighing. The other three fractions were oily liquids of somewhat variable composition. Only the first of these eluted from the column contained an appreciable amount of chlorine, its composition corresponding to an empirical formula ranging from C_7H_5Cl to C_8H_7Cl . It was found that the carbon/hydrogen ratio of the oils decreased with order of elution; this suggests that, while the first component eluted has much of the aromatic structure intact, the degree of aromatization decreases in the later fractions. The ultra-violet spectra of these oils were examined, but it was unfortunately not possible to characterize any of their constituents in this way.

RESULTS

GENERAL KINETIC CHARACTERISTICS

With a contact time of 0.3 sec and at a pressure of 12 mm, it was found that pyrolysis of chlorobenzene becomes detectable at 740° C; at 770° C and under these conditions the extent of decomposition is about 3 %.

The velocity constants k were determined by application of the first-order equation:

$$k = \frac{2 \cdot 303}{t_c} \log_{10} \frac{a}{a - x},$$
 (i)

where t_c is the contact time,* *a* is the total weight of chlorobenzene used up during a run and (a - x) is the weight of unchanged chlorobenzene recovered. The use of eqn. (i) is based on the assumption that diffusion is negligible,⁹ and that no volume change takes place due to reaction; the latter condition is probably fairly well satisfied on account of the very small extent of decomposition (generally 3-7 %) during a given run. Eqn. (i) has been applied to flow systems by Pease and Durgan,¹⁰ Barton,¹¹ and Barton, Head and Williams.¹²

The first-order velocity constant k calculated according to eqn. (i) decreases only slightly with initial chlorobenzene pressure p_0 (table 1); the approximate obedience to a first-order kinetic law is in agreement with the results of Cullis and Priday.¹ k is also sensibly independent of contact time over the range studied (table 2); this suggests that, under the conditions used, the reactant acquires the furnace temperature within a time shorter than the lowest value of the contact time.

| | | | Та | BLE 1 | | | |
|--------------------------|-------|-------|-------|-----------|-------|-------|-------|
| | | | Temp | o. 810° C | | | |
| p 0 (mm) | 6.0 | 8.5 | 11.2 | 12.8 | 15.6 | 18.7 | 21.5 |
| k (sec ⁻¹) | 0.159 | 0.158 | 0.152 | 0.150 | 0.148 | 0.148 | 0.145 |
| | | | TA | ble 2 | | | |
| | | | Temp | o. 818° C | | | |
| $t_{\rm c}$ (sec) 0.50 | | 0.50 | 1.32 | 2.51 | 3.17 | | 3.75 |
| $k (\text{sec}^{-1})$ (| | 0.200 | 0.191 | 0.198 | 0.193 | | 0.195 |

INFLUENCE OF TEMPERATURE

The variation of rate with temperature is shown in fig. 2. Between 770 and 830° C, there is a linear relationship between $\log_{10} k$ and 1/T. At *ca.* 830° C, there is, however, a sharp discontinuity and in the range 830-850° C the results, although not readily reproducible, show that the rate decreases markedly with temperature. At higher temperatures, the rate again increases. In the low temperature region, the apparent activation energy is 82 kcal mole⁻¹ in good agreement with the value determined by Cullis and Priday.¹

The influence of temperature on product yields (expressed as moles per mole of chlorobenzene decomposed) is shown in fig. 3. As the temperature is raised, the yields of hydrogen chloride and hydrogen (fig. 3(a)) pass through a minimum and then increase again; the yield of hydrogen chloride finally rises to a constant value while that of hydrogen eventually starts to decrease again. The temperature at which a minimum occurs in the above product yields (*ca.* 830° C) corresponds roughly with that at which there is a break in the $\log_{10} k$ against 1/T plot. Similarly the temperature (*ca.* 850° C) at which the maximum yields are obtained is the same as that at which the reaction rate again starts to increase with temperature following the region of negative temperature coefficient. The yields of methane and of p: p'-dichlorodiphenyl (fig. 3(*b*)), although very much lower than those of hydrogen chloride and hydrogen, show a roughly parallel variation with temperature.

* The contact time is defined as the time taken for 1 ml of reactant vapour to pass through the bulk volume of the reaction vessel. The assumption is made that there is no pressure change during reaction; this is probably justifiable in view of the fact that the extent of decomposition was invariably small.



FIG. 2.-The influence of temperature on the rate of decomposition of chlorobenzene.



FIG. 3.—The influence of temperature on the yields of products formed during the decomposition of chlorobenzene.

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In the temperature range studied, it is possible to calculate both the weight of chlorine corresponding to the amount of chlorobenzene decomposed and the weight of combined chlorine found in the products (as hydrogen chloride, p:p'-dichlorodiphenyl and the first fraction eluted from the chromatographic column). The amount of chlorine accounted



FIG. 4.—The influence of temperature on the percentage loss of combined chlorine during the decomposition of chlorobenzene.



FIG. 5.—The influence of added hydrogen on the rate of decomposition of chlorobenzene and on the yields of hydrogen chloride obtained.

for varies between 50 % and 80 % and the percentage loss depends markedly on temperature (fig. 4). In the determination of hydrogen chloride, the aqueous alcoholic solution was always found to have a smell not characteristic of either hydrogen chloride or the solvent, and during the preliminary work, attempts were made to identify the substance responsible. Chemical tests proved the absence of both acetylene and ethylene,

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but the material trapped out with hydrogen chloride was shown by analysis of its infrared spectrum ¹³ to contain considerable quantities of vinyl chloride. If it is assumed that the total loss of chlorine is due solely to the formation of vinyl chloride, which is difficult to detect and estimate chemically, values for the yield of this compound may be deduced at different temperatures. The calculated yield of vinyl chloride is thus at a maximum when the other product yields are at a minimum, since the formation of vinyl chloride is presumably complementary to that of the other chlorine-containing compounds.

INFLUENCE OF ADDED HYDROGEN

Fig. 5 shows the variation of rate with temperature when hydrogen is mixed with the organic vapour. In contrast with the behaviour observed in the absence of added hydrogen (fig. 2), the plot of $\log_{10} k$ against 1/T is linear over the whole temperature range investigated. Under all conditions, the decomposition is considerably accelerated by the presence of hydrogen, although above a molar hydrogen/chlorobenzene ratio of 0.25 the rate is scarcely affected by the hydrogen pressure.

The reaction products were found to be qualitatively the same as those obtained in the absence of hydrogen. The molecular proportions of the products were, however, altered, and a small amount of the added hydrogen could not be recovered and was therefore presumed to have been chemically involved in the reaction. The yield of hydrogen chloride, in common with the overall rate of decomposition of chlorobenzene, increases continuously with temperature (fig. 5).

DISCUSSION

An unusual feature of the thermal decomposition of chlorobenzene is the variation of reaction rate with temperature, the behaviour encountered being similar to that found in the oxidation of certain organic vapours.¹⁴ The explanation of the observed temperature coefficient must be that there are two distinct modes of breakdown, one of which is, so to speak, superimposed on the other and "flares up" between certain temperature limits.

In the present system, the existence of two separate decomposition mechanisms is confirmed by the variation with temperature of the nature of the products. At low temperatures (770-800° C), the main products are hydrogen chloride and hydrogen together with smaller amounts of p:p'-dichlorodiphenyl, the majority of the chlorine being accounted for as hydrogen chloride. The formation of these products appears to result from a chain cycle involving the radicals, Cl and C₆H₄Cl. No diphenyl or monochlorodiphenyl is found so that it is evident that chlorophenyl radicals—and *not* phenyl radicals—play an important part in chain-propagation; the formation of p:p'-dichlorodiphenyl to the exclusion of all other isomers suggests that attack of chlorobenzene takes place preferentially at the *para*-position.¹⁵ The chain cycle appears to involve the following steps:

$$\begin{array}{ccc} C_6H_5Cl \longrightarrow C_6H_5 + Cl \\ Cl + C_6H_5Cl \longrightarrow HCl + C_6H_4Cl \\ C_6H_4Cl \longrightarrow Cl + H_2 + \text{solid residue} \\ 2C_6H_4Cl \longrightarrow ClC_6H_4 \cdot C_6H_4Cl \\ C_6H_5 \longrightarrow H_2 + \text{solid residue} \\ Cl \xrightarrow{\text{walls}} \frac{1}{2}Cl_2, \end{array}$$

none of which necessarily involves rupture of the benzene ring. On the contrary, reaction appears to consist effectively in the "stripping" of the attached atoms from the aromatic carbon skeleton. Methane, the only product which necessitates ring-breaking, may well be formed in small quantities by thermal decomposition of p: p'-dichlorodiphenyl.¹⁶

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At moderate temperatures (800-850° C), considerable quantities of vinyl chloride are formed and the yields of hydrogen chloride, hydrogen, methane and p: p'-dichlorodiphenyl all decrease. Between 820 and 835° C, vinyl chloride is the main chlorine-containing product. Its formation necessitates rupture of the aromatic ring and the rate of this reaction must increase more rapidly with temperature than the ring-stripping process which predominates at low temperatures. As the temperature is increased, the yield of vinyl chloride reaches a maximum and then starts to decrease with a simultaneous reduction in the rate of consumption of chlorobenzene. The negative temperature coefficient of reaction rate coincides with the temperature region in which formation of vinyl chloride falls off. If the decrease in the yield of vinyl chloride at high temperatures is due to the thermal instability of intermediates which at lower temperatures lead to the formation of this compound, then the concurrent decrease in rate of consumption of chlorobenzene indicates that these intermediates form vinyl chloride by attacking further chlorobenzene; in other words, the reactions must involve a chain cycle, in which, moreover, the chains are fairly long. The exact nature of the chemical processes occurring is difficult to establish, but it is reasonable to assume that the first step is the "breaking-open" of the aromatic ring. A C_2 fragment, which will presumably be C_2HCl or C_2H_2 is then split off. In order to account for the formation of vinyl chloride, it is necessary to assume that these fragments then stabilize themselves by adding on the elements of hydrogen or hydrogen chloride respectively. Since under the experimental conditions used, only a small proportion of the reactant suffers decomposition and little hydrogen chloride and hydrogen as such are present, most of the fragments must be stabilized by reaction with further chlorobenzene. In general, the species C_2HCl and C_2H_2 are less likely to be formed in their excited states (as biradicals) than in their ground states. Since acetylene has never been detected in the present system and is indeed usually only found in insignificant amounts in the products of pyrolysis of benzene,^{16, 17} it seems probable that the fragment C₂HCl is the active chain-carrier in the ringbreaking process. This in turn suggests that the aromatic ring tends to break in the neighbourhood of the chlorine atom. Thus the reaction cycle set up may, for example, take place according to the equations :

$$C_{6}H_{5}Cl$$

$$-CH = CH - CH = CH - CH = CCl - C_{2}HCl + solid residue$$

$$-CH = CH - CH = CH - CCl = CH - CCl = CH - CCl = CH - CCl + C_{6}H_{3}Cl$$

$$C_{2}HCl + C_{6}H_{5}Cl \rightarrow CH_{2} = CHCl + C_{6}H_{3}Cl$$

$$C_{6}H_{3}Cl \rightarrow C_{2}HCl + solid residue.$$

Unless some such chain cycle takes place, it is difficult to see why a further increase in temperature should decrease the rate of decomposition of chlorobenzene. If, however, the C_2HCl fragments are thermally unstable at higher temperatures —decomposing to give carbon and hydrogen chloride—the rate of consumption of reactant will decrease, as is observed experimentally.

At high temperatures (850-880° C), the ring-stripping mechanism presumably again becomes predominant, and the reaction rate once more has a positive temperature coefficient. There is then an increase in the yields of hydrogen chloride, hydrogen and p: p'-dichlorodiphenyl.

Studies of the pyrolysis of chlorobenzene in the presence of hydrogen were not sufficiently detailed to enable any definite suggestions to be put forward as to the mode of action of this gas. On the basis of the mechanism postulated, however, addition of hydrogen would be expected to have two opposing effects. As regards the ring-breaking process, hydrogen will tend to inhibit reaction, for it will stabilize C_2HCl fragments and thereby prevent attack of further chlorobenzene by such entities. On the other hand it will assist the ring-stripping

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reaction by delaying recombination of chlorine atoms at the walls; thus in the presence of hydrogen, a series of reactions such as

$$Cl + H_2 \longrightarrow HCl + H$$
$$H + C_6H_5Cl \longrightarrow H_2 + C_6H_4Cl$$
$$C_6H_4Cl \longrightarrow Cl + H_2 + \text{solid residue}$$

will tend to occur in preference to

 $Cl \xrightarrow{\text{walls}} \frac{1}{2}Cl_2.$

In agreement with the above hypothesis, comparison of the rates of decomposition of chlorobenzene in the presence of added hydrogen (fig. 5) and in its absence (fig. 2) shows clearly that the acceleration is most marked in those temperature regions where the ring-stripping mechanism is predominant.

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