454. *The Thermal Decomposition of the Chlorofluoromethanes.*

By A. B. TRENWITH and R. H. WATSON.

The thermal decomposition of the three fluorochloromethanes has been studied in an alumina vessel between 400° and 900° and at pressures of about one atmosphere. Stability increases with the proportion of fluorine in the molecule. Interpretation of the results is rendered difficult by reactions involving the alumina surface at higher temperatures. It is clear, however, that in every case the principal products of homogeneous pyrolysis are compounds containing one fluorine atom more and one less than the parent halogenocarbon together with chlorine. Mechanisms have been suggested to account for the formation of these products and others obtained in smaller yield.

THE chlorofluoromethanes are relatively unreactive. Ruff and Keim [1] found that they attacked sodium, barium, and magnesium at 600° and some of them at least react with other elements. Thus dichlorodifluoromethane has been shown, in these laboratories, to behave at 500° as a mild chlorinating agent towards tellurium, which is thereby converted into the dichloride.[2] Their thermal decomposition does not appear to have been studied and, as one of us has been associated with a corresponding investigation of tetrafluoroethylene,[3] it seemed useful to apply the methods there developed to these three

[1] Ruff and Keim, *Z. anorg. Chem.*, 1931, 201, 245.

[2] Aynsley, *J.*, 1953, 3016.

[3] Atkinson and Trenwith, *J.*, 1953, 2082.

compounds. Tetrafluoroethylene could be decomposed in a steel vessel without appreciable attack on the metal, but at the temperatures required to decompose the chlorofluoromethanes they were far too corrosive for metals or silica, and even the fused alumina eventually resorted to was not immune. This failure to find an inert reaction vessel has precluded a detailed study of the kinetics of the decomposition, but enough information has been gathered to yield a general picture of their thermal stability and mode of decomposition.

EXPERIMENTAL

Materials.—The chlorofluoromethanes (" arctons "), from Imperial Chemical Industries Limited, were received in cylinders.

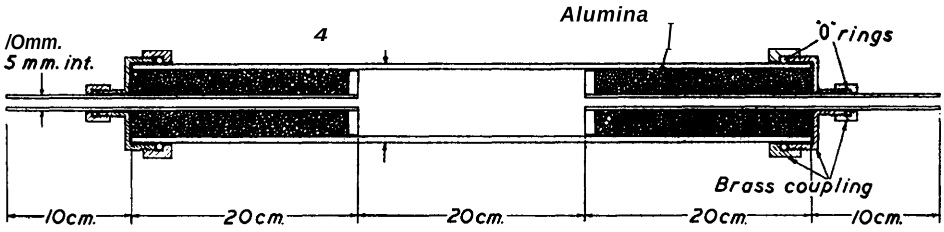
Chlorotrifluoromethane. The gas contained small amounts of carbon dioxide, oxygen, and nitrogen. The first was removed by passage through saturated aqueous potassium hydroxide followed by concentrated sulphuric acid; the second by means of a tower packed with activated copper on kieselguhr [4] at 200°; the nitrogen was ignored. Before use the gas was dried (P_2O_5).

Dichlorodifluoromethane. The carbon dioxide and oxygen were removed as before. A trace of high-boiling material was removed by passing the gas through a trap cooled to $-29°$.

Trichlorofluoromethane. This was condensed directly into the boiler of a Podbielniak-type fractionating column. After the removal of non-condensable matter by pumping, the condensable material was fractionated and a middle cut of the fraction boiling at 12°/500 mm. was retained

Apparatus.—This consisted of a purification train, a flow-meter, an alumina reaction vessel, collecting traps, a low-temperature Podbielniak-type distilling column and a bulb of accurately known volume for molecular-weight determinations. A mercury-vapour pump, backed by a rotary oil pump, was used to evacuate the apparatus which, except for the reaction vessel, was of Pyrex glass.

Several materials were tried for the reaction vessel. Silica was readily attacked giving silicon tetrafluoride and oxides of carbon, and metals gave volatile chlorides: only fused alumina proved satisfactory, and even this suffered some attack at the higher temperatures. Owing to the difficulty and cost of special fabrication in fused alumina, we were unable to have a normal form of reaction vessel and resorted to the method shown in the Figure whereby the centre portion of a fused alumina tube was converted into a reaction vessel by means of two circular plates of the same material. These fitted closely and had fused into them tubes which reached to the outside. Special adaptors were made to close both the wide and narrow tubes by means of compression rings. The reaction tube was heated in a tubular electric furnace controlled to ±1° by a " Sunvic " energy regulator. Temperatures were measured by means of a chromel–alumel thermocouple in a sheath between the reaction vessel and the furnace tube.



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Chlorotrifluoromethane

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train and flow-meter and into the reaction vessel, the cylinder valve being adjusted to give a steady flow at a pressure very near 1 atm. In order to allow the reaction to settle down, the products of pyrolysis formed during the first 15 min. of each run were pumped off, and the rest were collected in two traps cooled in liquid nitrogen. At the end of a run the pressure of non-condensable gas in the system was noted and, when necessary, this gas was analysed. The condensable products were transferred to the low-temperature column and analysed by fractional distillation. Where there was ambiguity, fractions were identified by molecular-weight determination, and sometimes by chemical or mass-spectrometric analysis.

Since trichlorofluoromethane boils at 23° its vapour could not be conveniently handled in the system at 1 atm., so a pressure of 400 mm. was employed. The material was drawn from a small storage bulb attached to the purification train through a tap; by adjusting this and the temperature of the bulb a steady flow of gas at the prescribed pressure was maintained.

Results.—Dichlorodifluoromethane. The decomposition was studied over the range 700—900°. Up to 800° the non-condensable gas was entirely nitrogen of equal amount to that obtained in a blank run with an unheated reaction vessel. At 850°, in addition to nitrogen, the non-condensable gases contained a small amount of carbon monoxide and at 900° this was appreciably greater and some carbon dioxide was also found, indicating an attack on the walls which was slight at 850° and increased with temperature. The gas itself was quite stable below 750° and almost completely decomposed at 900°. The principal products were chlorotrifluoromethane and chlorine; in addition there were smaller amounts of trichlorofluoromethane, carbon tetrachloride, a high-boiling liquid, and a white solid. The high-boiling liquid (b. p. ~115°) was a mixture with a carbon : fluorine : chlorine atomic ratio of 3 : 6 : 2, but the white solid contained very little chlorine (~3·5% w/w). Analysis enabled a balance of the carbon, fluorine, and chlorine to be struck which demonstrated the absence of measurable attack on the vessel below 850°, the atomic ratio carbon : fluorine : chlorine being almost exactly 1 : 2 : 2. The small deficiency of carbon and fluorine noticed at 850°, which became more pronounced at 900°, was presumably due to the formation of aluminium fluoride and oxides of carbon. The analyses are given in Table 1.

TABLE 1. *Products of pyrolysis of dichlorodifluoromethane.*

CF_2Cl_2 passed/hr. = 1·5 l.; pressure in reaction vessel = 760 mm.

Products (moles/100 moles of CF_2Cl_2 passed)

Temp.	CF_4	CF_3Cl	CF_2Cl_2	$CFCl_3$	CCl_4	Cl_2	$C_2F_4Cl_2$	High-b. p. liquid	White solid *
700°	—	—	100	—	—	—	—	—	—
750	—	1·5	96·2	0·4	—	2·7	0·2	—	—
800	1·1	10·7	73·4	4·9	1·3	11·9	—	0·8	95 g.
850	1·5	33·1	23·2	6·9	7·5	34·6	—	5·0	110 g.
900	2·0	31·2	6·1	5·8	4·7	50·6	—	3·0	300 g.

* g./100 moles of CF_2Cl_2 passed.

Chlorotrifluoromethane. The temperature range was 700—850°. The amount of non-condensable gas was always only slightly greater than that observed in a blank run, indicating the formation of very little carbon monoxide. Analysis of the condensable products showed the presence of appreciable quantities of carbon dioxide at all temperatures. This was substantiated by the shape of the plateaux at −83° in the curves of pressure of distillate against b. p., and by the difficulty experienced in fractionating the mixtures owing to vigorous bumping in the distillation column. The carbon dioxide was determined by passing the products, after distillation, through a tube packed with " Carbosorb " which removed both it and the chlorine. Subsequent fractionations produced distillation curves with shorter and more clearly defined plateaux at −83°, the decrease in length always being equivalent to the amount of carbon dioxide originally present. Mass-spectrometric analyses showed that the distillates at −83°, after the removal of carbon dioxide, were pure chlorotrifluoromethane.

The results are given in Table 2. The figures given for carbon tetrafluoride throughout this paper are probably slightly low, since, owing to its high vapour pressure, some must inevitably have been lost when removing the non-condensable gas.

As the proportionally large quantities of carbon dioxide indicate appreciable attack on the reaction vessel at all temperatures, it seemed unprofitable to use temperatures above 850°.

Trichlorofluoromethane. The temperature range was 440—745°. The gas begins to decompose at about 400° and, under the experimental conditions, decomposition was practically complete at 745°. Some surface reaction at 650° and above was indicated by the appearance of carbon monoxide in the non-condensable matter. No carbon dioxide was found at any temperature. The principal products were chlorine, carbon tetrachloride, and dichlorodifluoromethane; they were accompanied by a small amount of high-boiling liquid which was a mixture.

TABLE 2. *Products of pyrolysis of chlorotrifluoromethane.*

CF_3Cl passed/hr. = 2·25 l.; pressure in reaction vessel = 760 mm.

	Products (moles/100 moles of CF_3Cl passed)				
Temp.	CF_4	CF_3Cl	CF_2Cl_2	CO_2	Cl_2
706°	—	99·6	—	0·3	0·2
748	—	95·4	—	4·1	2·3
797	0·1	84·4	0·2	14·4	7·7
850	0·9	66·1	3·5	29·3	14·6

An analysis of the materials produced at 745° showed that a little of the carbon was missing; this is ascribed to the decomposition of some of the carbon tetrachloride formed into carbon and chlorine. The results are given in Table 3.

TABLE 3. *Products of pyrolysis of trichlorofluoromethane.*

$CFCl_3$ passed/hr. = 2·25 l.; pressure in reaction vessel = 400 mm.

	Products (moles/100 moles of $CFCl_3$ passed)					
Temp.	CF_3Cl	CF_2Cl_2	$CFCl_3$	CCl_4	Cl_2	High-b. p. liquid
440°	—	1·6	96·8	1·6	—	—
498	—	6·4	87·3	6·4	trace	—
603	—	15·9	44·4	26·4	13·0	3·6
650	—	18·0	25·5	30·8	26·0	6·7
705	—	12·2	18·1	27·2	48·7	9·9
745	1·1	8·0	13·5	23·9	70·1	10·9

DISCUSSION

This study of the pyrolysis of the chlorofluoromethanes, which has been inevitably complicated, at the higher temperatures, by reactions involving the surface of the vessel, indicates that their modes of decomposition are inherently complex. Nevertheless, general conclusions can be reached.

The chlorofluoromethanes are particularly stable and the stability increases with the fluorine : chlorine ratio. Thus although trichlorofluoromethane begins to decompose at 400°, both dichlorodifluoromethane and chlorotrifluoromethane are stable below 700°. The dichlorodifluoromethane is less stable than chlorotrifluoromethane, for at 850° approximately 80% is decomposed as compared with 40% of the chlorotrifluoromethane under comparable conditions.

In the pyrolysis of dichlorodifluoromethane the products probably arise from an initial splitting of a carbon–chlorine bond followed by reactions of the chlorine atom and radical formed with parent molecules. Most of the chlorine produced would then result from the reactions,

$$CF_2Cl_2 \longrightarrow CF_2Cl\cdot + Cl\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$Cl\cdot + CF_2Cl_2 \longrightarrow CF_2Cl\cdot + Cl_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

and other products could arise from two further reactions involving the transfer of either a fluorine or a chlorine atom from the parent molecule to a radical as shown :

$$CF_2Cl\cdot + CF_2Cl_2 \longrightarrow CF_3Cl + CFCl_2\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CFCl_2\cdot + CF_2Cl_2 \longrightarrow CFCl_3 + CF_2Cl\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

It is to be noted that where a fluorine-atom transfer is involved a chlorine-atom transfer can also be postulated and *vice versa*, but the alternatives will produce no net change in the system. Reactions (1)—(4) account for the three principal products of pyrolysis.

Above 700° chlorotrifluoromethane is unstable and trichlorofluoromethane even more so. Clearly the small amounts of secondary products may result from the subsequent decomposition of these primary ones. Thus decomposition of chlorotrifluoromethane could account for the small amounts of carbon tetrafluoride found and the carbon tetrachloride may result from that of trichlorofluoromethane. The formation of materials of high molecular weight may arise from radical recombination followed by the splitting off of a chlorine atom and further radical recombination (5—7). The trace of dichlorotetrafluoroethane produced at 750° indicates the occurrence of reaction (5) at this temperature, and the absence of this product at higher temperatures may be due to its low stability.

$$CF_2Cl\cdot + CF_2Cl\cdot \longrightarrow C_2F_4Cl_2 \qquad (5)$$

$$C_2F_4Cl_2 \longrightarrow C_2F_4Cl\cdot + Cl\cdot \qquad (6)$$

$$C_2F_4Cl\cdot + CF_2Cl\cdot \longrightarrow C_3F_6Cl_2 \qquad (7)$$

From chlorotrifluoromethane, by analogy, we should expect the principal products to be carbon tetrafluoride, dichlorodifluoromethane, and chlorine, all of which were obtained. The proportion of carbon dioxide also formed at all temperatures showed, however, that reaction with the walls of the vessel was considerable.

The pyrolysis of trichlorofluoromethane is of more interest since, in this instance, surface effects are too slight to confuse the issue. A mechanism similar to that already suggested would lead to dichlorodifluoromethane, carbon tetrachloride, chlorine, and some high-boiling material together with smaller quantities of chlorotrifluoromethane and carbon tetrafluoride. All of these were found with the exception of the last. Although at all temperatures used chlorine is the major product from dichlorodifluoromethane, with trichlorofluoromethane this is not so below 650°. At 500°, for example, only dichlorodifluoromethane and carbon tetrachloride appear in measurable quantity, and even at 600° they both exceed the chlorine produced. There appear to be two possible explanations for these observations: the first invokes the straightforward bimolecular reaction

$$2CFCl_3 \longrightarrow CF_2Cl_2 + CCl_4$$

concurrent with, but predominant over, the free-radical reactions at the lower temperatures; the second calls for a chain process in which reactions similar to (3) and (4) are the chain-carrying steps. With dichlorodifluoromethane the high proportion of chlorine formed precludes such chain reactions but with trichlorofluoromethane at the lower temperatures this restriction does not operate. Unfortunately the evidence is insufficient to allow us to decide between these alternatives, but since there is little to suggest a bimolecular reaction in the case of either chlorotrifluoromethane or dichlorodifluoromethane we are led to prefer the latter.

Inorganic Chemistry Laboratories,
King's College, Newcastle upon Tyne, 1.

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