401. *The Thermal Decomposition of Tetrafluoroethylene.*

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The thermal decomposition of systems derived from tetrafluoroethylene, occurring in a nickel vessel at temperatures from 550° to 750°, is described.

The tetrafluoroethylene–perfluoro*cyclo*butane equilibrium mixture decomposes at temperatures above 550° forming perfluoropropene by a first-order mechanism. This in turn decomposes giving perfluoro*iso*butene in a reaction with an order of 1·5. A reaction scheme, based on the difluoromethylene radical as intermediate, is shown to be in accord with the experimental results.

At temperatures above 700° perfluoro*iso*butene is shown to disproportionate giving perfluoroethane and various non-volatile products by a first-order mechanism. A reaction scheme, based on the trifluoromethyl radical, is suggested.

RESULTS reported by Miller [1] and Atkinson and Trenwith [2] show that the thermal decomposition of tetrafluoroethylene can be divided into three phases. At low temperatures perfluoro*cyclo*butane is the main product; at medium temperatures perfluoropropene and a perfluorobutene are produced; and at high temperatures perfluoroethane is formed.

Atkinson and Trenwith also performed a detailed investigation between 300° and 590°, showing that a reversible cyclic dimerisation occurs:

$$2CF_2{:}CF_2 \longrightarrow (CF_2)_4,\ k_1 = 10{\cdot}3 \times 10^7 \exp(-25{,}400/\boldsymbol{R}T)\ \text{l. mole}^{-1}\ \text{sec.}^{-1} \quad . \quad (1)$$

$$(CF_2)_4 \longrightarrow 2CF_2{:}CF_2,\ k_2 = 8{\cdot}9 \times 10^{15} \exp(-74{,}100/\boldsymbol{R}T)\ \text{sec.}^{-1} \quad . \quad . \quad (2)$$

Their values for rate constants are substantially in agreement with those of Lacher, Tompkin, and Park [3] for reaction (1) and those of Gray and Pritchard [4] for reaction (2). No detailed investigation of the formation of perfluoropropene, perfluorobutene, and perfluoroethane has hitherto been made.

The work of Brice *et al.*[5] has proved that the perfluorobutene produced was perfluoro*iso*butene and not perfluorobut-1-ene as Miller, and Atkinson and Trenwith, had assumed.

EXPERIMENTAL

Materials.—(a) *Tetrafluoroethylene.* The gas, from a small cylinder, was first stored over water to remove hydrogen chloride and then fractionated in a low-temperature (Podbielniak) distillation column. Its purity was checked by its infrared spectrum.

(b) *Perfluoroethane, perfluoropropene, perfluoro*cyclo*butane, and perfluoro*iso*butene.* The products of several pyrolyses, performed under conditions appropriate for the production of the required material, were amalgamated and that material was fractionally distilled. A second fractionation was performed to purify the material, and the purity was checked by infrared spectroscopy.

Pyrolyses of Fluorocarbons.—(a) *Apparatus.* All pyrolyses were performed by static methods. The gas to be pyrolysed was introduced into a cylindrical (10 in. long, 2 in. o.d.) reaction vessel set in a horizontal tubular wire-wound furnace with an electronic control of the type described by Roberts,[6] which kept the temperature constant to within ±0·5°. The temperature of the reaction vessel was measured by a chromel–alumel thermocouple in a coaxial well traversing almost the entire length of the reaction vessel. The capillary inlet tube was connected to a capillary manometer, by which changes in total pressure were followed to

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[1] Miller, "Preparation and Technology of Fluorine and Organic Fluorine Compounds," National Nuclear Energy Series, Vol. VII, 1951, chap. 32.

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

[3] Lacher, Tompkin, and Park, *J. Amer. Chem. Soc.*, 1952, **74**, 1693.

[4] Gray and Pritchard, *J.*, 1956, 1002.

[5] Brice, La Zerte, Hals, and Pearlson, *J. Amer. Chem. Soc.*, 1953, **75**, 2698.

[6] Roberts, *Electronic Engineering*, 1951, **23**, 51.

the nearest 0·5 mm. Reaction vessels of stainless steel (En. 58B) and nickel were used. Since oxide scale was shown to interfere with the pyrolyses, the steel vessel was welded by the argon-arc technique to minimise scaling, and both the steel and the nickel vessels were filled with tetrafluoroethylene and left at 650° overnight to remove any traces of oxide formed during welding.

(b) *Procedure.* A series of pyrolyses with a common initial reactant pressure were performed at a given temperature, and each member was terminated after a different time. The volatile materials in the system were measured by infrared methods.

Infrared Analysis.—A Grubb–Parsons double-beam spectrometer was used and calibration curves for each pure standard gas were drawn.

Trace compounds, when suspected, were characterised by amalgamating the products of several identical pyrolyses, performing a fractionation, and subjecting suspect fractions to infrared analysis. The identities of these compounds were established by reference to either Bricė *et al.*[5] or the American Petroleum Institute " Catalog of Infra-Red Spectral Data," where the established spectra of all the fluorocarbon gases likely to be encountered are recorded. These sources were also used to show which lines could be used for the estimation of each product.

Perfluoro*cyclo*propane and perfluorobut-1-ene (uniquely characteristic lines at 11·6 μ and 10·6 μ respectively) were never encountered. Perfluorobut-2-ene (uniquely characteristic line at 11·3 μ) was found in traces. Carbon tetrafluoride and perfluoropropane share a characteristic line at 7·9 μ. Both compounds appear as minute traces, perfluoropropane being produced at medium temperatures and carbon tetrafluoride at high temperatures.

Tetrafluoroethylene, perfluoroethane, perfluoropropene, perfluoro*cyclo*butane, and perfluoro*iso*butene were the most important compounds in the pyrolyses investigated, comprising over 99% of the volatile materials analysed in each case. Of these, perfluoro*cyclo*butane and perfluoro*iso*butene had uniquely characteristic lines at 10·45 μ and 10·05 μ respectively. The line at 5·6 μ was used for the estimation of perfluoropropene, because the only other compound which it characterised, perfluorobut-1-ene, was never detected in the system. The triplet at 9·0 μ had to be used for the estimation of perfluoroethane, although the trace products carbon tetrafluoride and perfluorobut-2-ene also had lines in this region. All the above lines had distinct resolution, free from overlap by the lines of other of the major products, and the compounds could be estimated to within 1%.

The 8·45 μ line used for the estimation of the parent compound, tetrafluoroethylene, was the least satisfactory since it overlapped the 8·4 μ line of perfluoro*iso*butene and the 8·5 μ line of perfluoropropene, both major products. The extrapolation necessary in the estimation of tetrafluoroethylene reduced the accuracy to ±5%. Fortunately, it transpired that although tetrafluoroethylene was an important intermediate at medium temperature, it was not necessary to base any detailed calculations on the variation of the tetrafluoroethylene pressure.

RESULTS

Pyrolyses in Nickel.—Homogeneous gas-phase reactions occurred. Figs. 1 and 2 show the results obtained from the pyrolyses of tetrafluoroethylene and perfluoro*cyclo*butane at 650° and 700° respectively. They show that four reactions successively produce perfluoro*cyclo*butane, perfluoropropene, perfluoro*iso*butene, and perfluoroethane from tetrafluoroethylene.

Low-temperature phase. The first reaction in the series, that producing perfluoro*cyclo*butane, occurs at temperatures above 300° and has been adequately investigated by Atkinson and Trenwith.[2] The results obtained for pyrolyses at temperatures above 550° substantially confirm their conclusions.

Medium-temperature phase. Fig. 1 clearly shows that the second reaction is that producing perfluoropropene, and not the perfluorobutene as Trenwith [7] suggests. The reactant is evidently the tetrafluoroethylene–perfluoro*cyclo*butane equilibrium mixture produced quickly by reactions (1) and (2), so it was investigated with each of these compounds as starting material. Series of pyrolyses of tetrafluoroethylene were performed at 600° and 650° and of perfluoro*cyclo*butane at 550°, 575°, 600°, and 650° (see Figs. 1, 2, and 3). The results from the two series performed at 600° were identical. Graphs of log d$[C_4F_8]$/d*t* against log $[C_4F_8]$ showed the reaction to be of the first order in perfluoro*cyclo*butane.

Fig. 1 also shows that perfluoro*iso*butene is not produced until an appreciable quantity of

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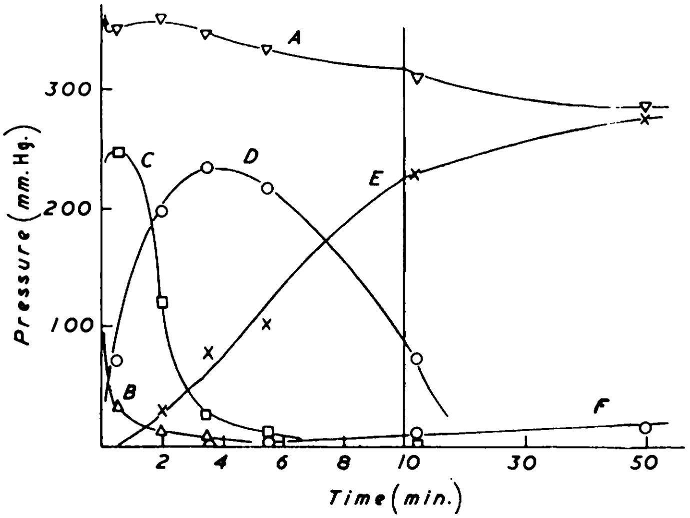
[7] Trenwith, Ph.D. Thesis, London, 1952.

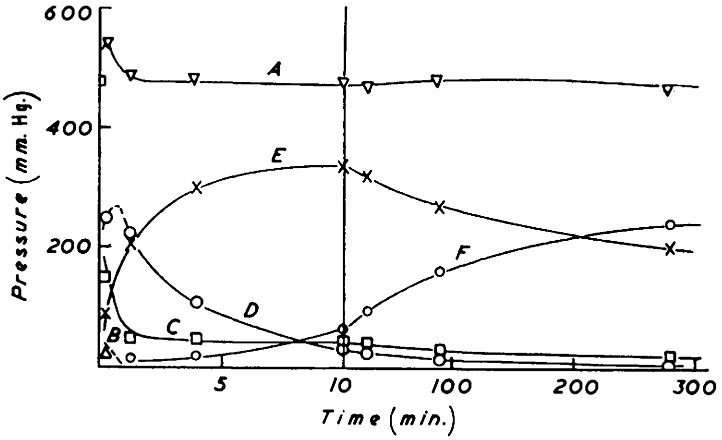
perfluoropropene has been formed. It was therefore assumed that the bulk of the *iso*butene was formed from the propene. The reaction producing perfluoro*iso*butene was therefore investigated by pyrolysing perfluoropropene at 600°, 625°, 650°, and 675° (Fig. 4). It was found that the reaction had an order of 1·5. Certain small material losses were noted. It is suggested that these might be associated with a white dust that settled in the cooler parts of the system.

FIG. 1. *Pyrolysis of tetrafluoroethylene at* 650°.



A, Total pressure; *B*, tetrafluoroethylene; *C*, perfluoro*cyclo*butane; *D*, perfluoropropene; *E*, perfluoro*iso*butene; *F*, perfluoroethane.

FIG. 2. *Pyrolysis of perfluoro*cyclo*butane at* 700°.



A, Total pressure; *B*, tetrafluoroethylene; *C*, perfluoro*cyclo*butane; *D*, perfluoropropene; *E*, perfluoro*iso*butene; *F*, perfluoroethane.

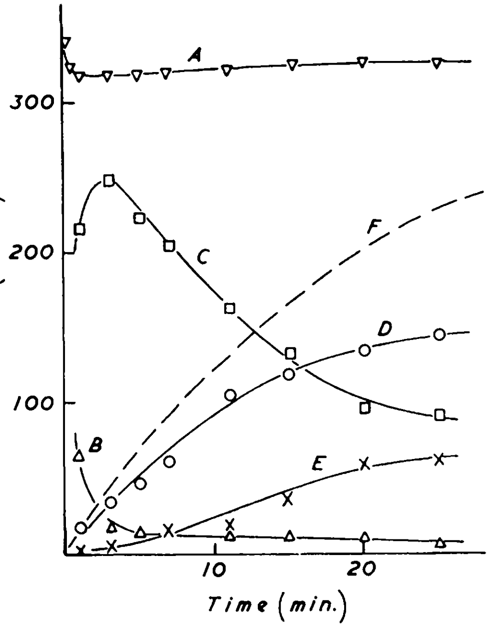
High-temperature phase. Fig. 2 clearly shows that the perfluoroethane is formed at 700° when the only major reactant is perfluoro*iso*butene. It is therefore assumed that most, if not all, of the perfluoroethane is produced from perfluoro*iso*butene. The pyrolysis of perfluoro*iso*butene at 700°, 725°, and 750° was investigated (see Fig. 5). The reaction was found to be of the first order.

During these pyrolyses the total pressure remained virtually constant (see Fig. 5) showing that the overall reaction must have been :

$$(CF_3)_2C{:}CF_2 \longrightarrow CF_3{\cdot}CF_3 + \text{non-volatile materials} \quad . \; . \; . \; . \; . \quad (3)$$

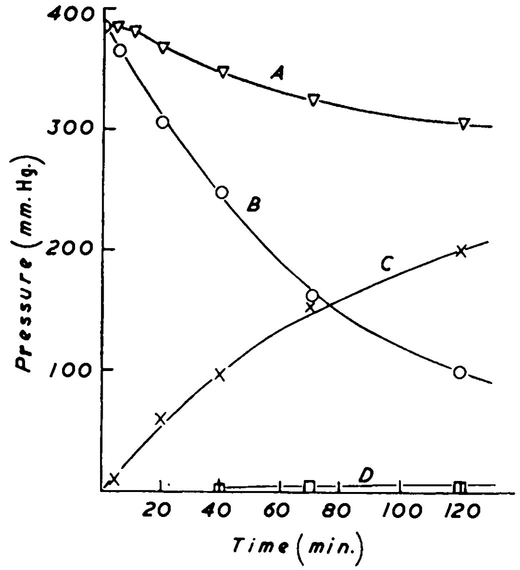
The non-volatile materials proved separable into grey and dark-red solids. Organic microanalysis showed that both solids had approximate formulæ C_5F_4. Since the overall composition of the non-volatile materials in equation (3) should be CF, a certain amount of fluorine may have been lost by reaction with the nickel vessel. The dark-red solid was insoluble in water, but readily soluble in organic solvents. It absorbed heavily in the blue and ultraviolet regions, as does perfluorobutadiene.[8] The infrared spectrum of the red solid was generally indeterminate but a sharp peak at 5·75 μ was ascribed to the fluorocarbon C:C double bond. The line characteristic of this bond is found at 5·56 μ in the perfluoroalk-1-enes and shifts to higher wavelengths for conjugated compounds (*e.g.*, 5·65 for perfluorobutadiene [8]). It was concluded that the red solid was a complex mixture of highly conjugated unsaturated fluorocarbons of relatively high molecular weight. The grey solid, insoluble in all common reagents, was probably a mixture of elementary carbon and some high-molecular weight fluorocarbon. It is thought to represent the final degradation product of the conjugated compounds.

FIG. 3. *Pyrolysis of tetrafluoroethylene at* 600°.



A, Total pressure; *B*, tetrafluoroethylene; *C*, perfluoro*cyclo*butane; *D*, perfluoropropene; *E*, perfluoro*iso*butene; *F*, calculated pressure of perfluoropropene if no decomposition to perfluoro*iso*butene.

FIG. 4. *Pyrolysis of perfluoropropene at* 600°.



A, Total pressure; *B*, perfluoropropene; *C*, perfluoro*iso*butene; *D*, octafluoro*cyclo*butane.

Pyrolyses in Stainless Steel.—The pyrolysis of tetrafluoroethylene or perfluoro*cyclo*butane in steel resulted, after the establishment of the equilibrium between tetrafluoroethylene and octafluoro*cyclo*butane, in a slowly decelerating pressure decrease virtually to zero. This was just noticeable in pyrolyses at 600°, but quite appreciable at 650°. Analysis of the volatile matter involved showed that perfluoropropene and perfluoro*iso*butene were being formed, just as with similar pyrolyses in the nickel vessel.

The pyrolyses of perfluoropropene and perfluoro*iso*butene in steel resulted in the same pressure decrease virtually to zero, occurring at appreciable rates at temperatures as low as

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[8] Haszeldine, *J.*, 1952, 4423.

450°. The rate of the reaction was not reproducible; successive runs became slower and slower unless the steel vessel was evacuated at 800° for several hours between each run.

The products of these pyrolyses were grey-black flakes whose organo-carbon content was 98% carbon. The inorganic content, soluble in dilute hydrochloric acid, was fluorides of manganese, iron, and chromium. The nickel and titanium components of the stainless steel were not attacked.

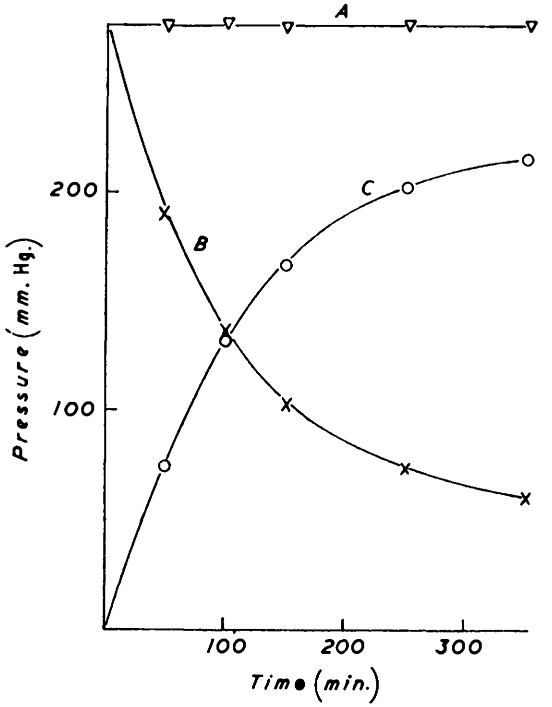

FIG. 5. *Pyrolysis of perfluoro*iso*butene at* 725°.

A, Total pressure; *B*, perfluoro*iso*butene; *C*, perfluoroethane.

The reaction was thus a heterogeneous attack on the steel vessel. The carbon and fluoride coat forming on the walls of the vessel impeded further attack. The peeling-off of this coat (and therefore the attack) was accelerated by high temperatures.

DISCUSSION

The Reaction producing Perfluoropropene.—It is desirable to consider a reaction scheme that would cover the first-order reaction producing perfluoropropene from the tetrafluoroethylene–perfluoro*cyclo*butane equilibrium mixture. The reaction scheme now suggested is based on difluoromethylene because this radical is known to exist [9] and reaction schemes based on other radicals would be expected to produce appreciable quantities of saturated compounds, for which there is no experimental evidence.

Tetrafluoroethylene and perfluoro*cyclo*butane are both possible reactants; it is possible to derive two alternative schemes for the two possible reactants that fit the kinetic evidence recorded above.

In the first scheme perfluoropropene and difluoromethylene are formed by the dissociation of perfluoro*cyclo*butane :

$$\mathrm{2CF_2{:}CF_2 \longrightarrow (CF_2)_4} \tag{1}$$

$$\mathrm{(CF_2)_4 \longrightarrow 2CF_2{:}CF_2} \tag{2}$$

$$\mathrm{(CF_2)_4 \longrightarrow CF_3{\cdot}CF{:}CF_2 + CF_2} \tag{4}$$

$$\mathrm{CF_2 + CF_2{:}CF_2 \longrightarrow CF_3{\cdot}CF{:}CF_2} \tag{5}$$

$$\mathrm{CF_3{\cdot}CF{:}CF_2 \longrightarrow CF_2{:}CF_2 + CF_2} \tag{6}$$

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[9] Atkinson, *J.*, 1952, 2684.

If it is assumed that a stationary state is attained where the difluoromethylene concentration is constant, then,

$$k_4[(CF_2)_4] = k_5[CF_2][C_2F_4] - k_6[CF_3{\cdot}CF{:}CF_2] \quad . \ . \ . \ . \ . \ . \quad (7)$$

and, if k_6 is small,

$$d[CF_3{\cdot}CF{:}CF_2]/dt = 2k_4[(CF_2)_4] \quad . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

Also,

$$4d[(CF_2)_4]/dt + 2d[C_2F_4]/dt = -\ 3d[CF_3{\cdot}CF{:}CF_2]/dt \quad . \ . \ . \quad (9)$$

whence

$$2d[(CF_2)_4]/dt + d[C_2F_4]/dt = -\ 3k_4[(CF_2)_4] \quad . \ . \ . \ . \ . \ . \quad (10)$$

$$2 \ln [(CF_2)_4] + \int\{d[C_2F_4]/[(CF_2)_4]\} = 3k_4t + \text{Constant} \quad . \ . \ . \ . \quad (11)$$

In order to proceed further with this fundamental equation it is necessary to make the further assumption that the basic tetrafluoroethylene–perfluoro*cyclo*butane equilibrium is attained rapidly compared with subsequent reactions, and that these subsequent reactions do not greatly disturb the equilibrium, *i.e.*, that

$$k_1[C_2F_4]^2 = k_2[(CF_2)_4] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (12)$$

whence

$$2 \ln [(CF_2)_4] - (k_2/\{k_1[(CF_2)_4]\})^{\frac{1}{2}} = -\ 3k_4t + \text{Constant} \quad . \ . \ . \ . \quad (13)$$

Table 1 shows values of k_4 derived from equations (8) and (13). From these values the following Arrhenius equation was derived

$$k_4 = 3{\cdot}9 \times 10^{16} \exp(-79{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}. \quad . \ . \ . \ . \ . \ . \quad (14)$$

TABLE 1.

Temperature	550°	575°	600°	625°	650°
10^6k_4 (sec.$^{-1}$) from eqn. (8)	50	200	633	2960	8570
10^6k_4 (sec.$^{-1}$) from eqn. (13)	60	260	660	4000	9440

A second scheme based on the association of two tetrafluoroethylene molecules is equally likely on kinetic grounds :

$$2CF_2{:}CF_2 \longrightarrow (CF_2)_4 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$(CF_2)_4 \longrightarrow 2CF_2{:}CF_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$2CF_2{:}CF_2 \longrightarrow CF_3{\cdot}CF{:}CF_2 + CF_2;\ d[C_2F_4]dt = -\ k_{15}[C_2F_4]^2 \quad . \quad (15)$$

$$CF_2 + CF_2{:}CF_2 \longrightarrow CF_3{\cdot}CF{:}CF_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$CF_3{\cdot}CF{:}CF_2 \longrightarrow CF_2{:}CF_2 + CF_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

If this is treated exactly as the previous scheme, it is possible to derive

$$d[CF_3{\cdot}CF{:}CF_2]/dt = [(CF_2)_4]k_{15}k_2/k_1 \quad . \ . \ . \ . \ . \ . \quad (16)$$

and

$$2 \ln [(CF_2)_4] - (k_2/k_1[(CF_2)_4])^{\frac{1}{2}} = -\ 1{\cdot}5\ k_{15}k_2t/k_1 + \text{constant} \quad . \ . \quad (17)$$

By comparison with eqns. (8) and (13) it can be seen that

$$k_{15} = 2k_1k_4/k_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (18)$$

From equations (1), (2), (14), and (18) it can be calculated that

$$k_{15} = 9{\cdot}0 \times 10^8 \exp(-30{,}300/\boldsymbol{R}T) \text{ l. mole}^{-1} \text{ sec.}^{-1} \quad . \ . \ . \quad (19)$$

It is possible to adjudicate between the two schemes outlined above by considering the circumstances at 500°. It can be calculated that at 500° and 400 mm.

$$\text{Rate (1)} = 4{\cdot}7 \times 10^{-4} \text{ mole l.}^{-1} \text{ sec.}^{-1} \qquad (20)$$

$$\text{Rate (2)} = 8{\cdot}3 \times 10^{-8} \text{ mole l.}^{-1} \text{ sec.}^{-1} \qquad (21)$$

$$\text{Rate (4)} = 1{\cdot}5 \times 10^{-8} \text{ mole l.}^{-1} \text{ sec.}^{-1} \qquad (22)$$

$$\text{Rate (15)} = 1{\cdot}7 \times 10^{-4} \text{ mole l.}^{-1} \text{ sec.}^{-1} \qquad (23)$$

If reaction (4) represents the true reaction path then the pyrolysis of tetrafluoroethylene at 500° should yield little or no perfluoropropene, because not only is (4) the slowest reaction, but it must await the build-up of perfluoro*cyclo*butane by reaction (1) before it can commence. If reaction (15) is correct, then the pyrolysis of tetrafluoroethylene at 500° should readily yield perfluoropropene since reaction (1) is only about three times as fast as reaction (15). Tetrafluoroethylene at 430 mm. pressure was pyrolysed for 20 sec. at 500°. No perfluoropropene was found when the products were subjected to infrared analysis; they contained 38·5% of perfluoro*cyclo*butane, which corresponds to dimerisation of 55·5% of the original tetrafluoroethylene. If the second reaction scheme, involving reaction (15), were the true reaction path for formation of perfluoropropene, about 15% of this compound would have been found in the products. It is concluded that the first scheme, involving reaction (4), represents the true reaction path.

*The Reaction producing Perfluoro*iso*butene.*—Any reaction scheme put forward has to explain (*a*) the production of perfluoro*iso*butene from perfluoropropene by a reaction of order 1·5 and (*b*) the existence of an apparent induction period in the total-pressure curve; the initial rate was less than the maximum rate (Fig. 4). The ready production of perfluoro*iso*butene with perfluoropropene from perfluoro*cyclo*butane or tetrafluoroethylene (Fig. 3) suggests that the intermediates in both pyrolyses are identical. Further evidence for this supposition was found in that the pyrolysis of pure perfluoropropene at 600° for 40 minutes or more produced detectable quantities (about 1%) of perfluoro*cyclo*butane, which must have been in equilibrium with tetrafluoroethylene and difluoromethylene by reactions (2) and (4). Accordingly the following mechanism involving tetrafluoroethylene and difluoromethylene was derived:

$$CF_3{\cdot}CF{:}CF_2 \longrightarrow CF_2{:}CF_2 + CF_2 \qquad (6)$$

$$CF_2{:}CF_2 + CF_2 \longrightarrow CF_3{\cdot}CF{:}CF_2 \qquad (5)$$

$$CF_2 + CF_3{\cdot}CF{:}CF_2 \longrightarrow (CF_3)_2C{:}CF_2 \qquad (24)$$

$$CF_2{:}CF_2 + CF_3{\cdot}CF{:}CF_2 \longrightarrow (CF_3)_2C{:}CF_2 + CF_2 \qquad (25)$$

If it is assumed that a steady state is obtained at which the difluoromethylene and tetrafluoroethylene concentrations are constant, then

$$k_6[CF_3{\cdot}CF{:}CF_2] + k_{25}[C_2F_4][CF_3{\cdot}CF{:}CF_2] = k_5[C_2F_4][CF_2] + k_{24}[CF_3{\cdot}CF{:}CF_2][CF_2] \qquad (26)$$

$$k_6[CF_3{\cdot}CF{:}CF_2] = k_5[C_2F_4][CF_2] + k_{25}[CF_3{\cdot}CF{:}CF_2][C_2F_4] \qquad (27)$$

Whence

$$2k_{25}[C_2F_4][CF_3{\cdot}CF{:}CF_2] = k_{24}[CF_3{\cdot}CF{:}CF_2][CF_2] \qquad (28)$$

If, in addition, it is assumed that the molecule–molecule reaction (25) is much slower than the molecule–radical reaction (5), *i.e.*,

$$k_{25}[C_2F_4][CF_3{\cdot}CF{:}CF_2] \ll k_5[C_2F_4][CF_2] \qquad (29)$$

then

$$k_6[CF_3{\cdot}CF{:}CF_2] = k_5[C_2F_4][CF_2] \qquad (30)$$

From equations (28) and (30)

$$[CF_2]^2 = [CF_3{\cdot}CF{:}CF_2]2k_6k_{25}/k_5k_{24} \qquad (31)$$

It can further be shown that

$$-\mathrm{d}[\mathrm{CF_3{\cdot}CF{:}CF_2}]/\mathrm{d}t = 1{\cdot}5[\mathrm{CF_3{\cdot}CF{:}CF_2}]^{3/2}\sqrt{(2k_6k_{24}k_{25}/k_5)} \quad . \quad . \quad . \quad (32)$$

The assumption in equation (29) implies that equilibrium between reactions (5) and (6) is almost established before the other reactions have taken place to any noticeable extent. If we predict also that k_{25} is markedly less than k_{24} the apparent induction period can be explained. At first C_2F_4 and CF_2 are formed in equal amounts and are lost in equal amounts by reaction (5) but CF_2 is also lost by reaction (24) whilst little C_2F_4 is lost by reaction (25). At this stage the effective reaction is

$$2\mathrm{CF_3{\cdot}CF{:}CF_2} = \mathrm{C_2F_4} + \mathrm{(CF_3)_2C{:}CF_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and there is no change in volume. Reaction (25) becomes increasingly significant as the C_2F_4 accumulates, until the steady state to which equation (32) refers is established.

Integration of eqn. 32 leads to

$$1/\sqrt{([\mathrm{CF_3{\cdot}CF{:}CF_2}])} = (3t/4)\sqrt{(2k_6k_{24}k_{25}/k_5)} + \text{Constant} \quad . \quad . \quad . \quad (34)$$

Values of $\sqrt{(k_6k_{24}k_{25}/k_5)}$ for the various pyrolysis series, obtained from application of eqn. (34) are given in Table 2.

TABLE 2.

Temperature	600°	625°	650°	675°
$10^5\sqrt{(k_6k_{24}k_{25}/k_5)}$ (l.$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-1}$)	159	447	869	2100

From these values an Arrhenius equation was derived,

$$\sqrt{(k_6k_{24}k_{25}/k_5)} = 3{\cdot}4 \times 10^{10} \exp(-53{,}500/\boldsymbol{R}T)\ \text{l.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1} \qquad (35)$$

Since reactions (5) and (24) are very similar, each involving the addition of a difluoromethylene radical to a simple perfluoro-olefin, we can assume them to have similar values for activation energy and frequency factor, whence

$$E_6 + E_{25} = 107\ \text{kcal./mole} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$\sqrt{(A_6A_{25})} = 3{\cdot}4 \times 10^{10}\ \text{l.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (37)$$

It is instructive to compare reaction (25) with reaction (1). It can be calculated that at 400°

$$\text{Rate (1)} = 0{\cdot}5[\mathrm{C_2F_4}]^2\ \text{mole l.}^{-1}\ \text{sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

An equimolecular mixture of tetrafluoroethylene and perfluoropropene was pyrolysed at 400° in order to permit reactions (1) and (25) to compete. No perfluoro*iso*butene was detectable by infrared methods, so reaction (1) must have been at least 100 times faster than reaction (25), *i.e.*,

$$k_{25} \leqslant 5 \times 10^{-3}\ \text{l. mole}^{-1}\ \text{sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

If, on the basis of structural similarity, we assign similar frequency factors to reactions (1) and (25), then

$$A_{25} = 10^8\ \text{l. mole}^{-1}\ \text{sec.}^{-1} \quad E_{25} \geqslant 32\ \text{kcal./mole} \quad . \quad . \quad . \quad (40)$$

$$A_6 = 10^{13}\ \text{sec.}^{-1} \quad E_6 \leqslant 75\ \text{kcal./mole} \quad . \quad . \quad . \quad (41)$$

The activation energies in reactions (2), (4), and (6) are similar, probably because they all involve the breaking of a C–C single bond as the first step. If this is the case, then we should expect these activation energies to exceed the value of D(C–C) for fluorocarbons. This must be taken as evidence favouring Rabinovitch and Reed's value of D(C–C) = 62 kcal.[10] and against Dibeler, Reese, and Mohler's value of 124 kcal.[11] The unusually high frequency factors in (2) and (4) are a feature of ring-opening reactions.

The small material losses and the dust obtained may be ascribed to polymerisation. Atkinson[9] has shown that difluoromethylene can initiate the gas-phase polymerisation of tetrafluoroethylene. Atkinson and Trenwith[2] and Gray and Pritchard[4] reported that the attack of the tetrafluoroethylene pyrolysis system on silica occurs at 550° and above. It is concluded that the attack is probably by the difluoromethylene radical which is then present.

*The Disproportionation of Perfluoro*iso*butene producing Perfluoroethane.*—The reaction scheme to be suggested must explain the first-order kinetics, the production of one molecule of perfluoroethane per molecule of reactant destroyed, and the production of conjugated high-molecular weight fluorocarbons. Since perfluoroethane is the major product it is assumed that trifluoromethyl is the most likely intermediate. The following scheme is suggested:

$$(CF_3)_2C{:}CF_2 \longrightarrow CF_3 + CF_3{\cdot}CF{:}CF \quad . \; . \; . \; . \; . \quad (42)$$

$$CF_3 + (CF_3)_2C{:}CF_2 \longrightarrow CF_3{\cdot}CF_3 + CF_3{\cdot}CF{:}CF \quad . \; . \; . \; . \quad (43)$$

$$CF_3{\cdot}[CF{:}CF]_n + CF_3{\cdot}[CF{:}CF]_m \longrightarrow CF_3{\cdot}[CF{:}CF]_{n+m} + CF_3 \quad . \; . \; . \quad (44)$$

$$CF_3{\cdot}[CF{:}CF]_p + CF_3{\cdot}[CF{:}CF]_q \longrightarrow CF_3{\cdot}[CF{:}CF]_{p+q}{\cdot}CF_3 \quad . \; . \; . \; . \quad (45)$$

If M represents $CF_3{\cdot}[CF{:}CF]_r$, where r is any positive integer, and if it is assumed that in the stationary state the concentrations of the intermediates CF_3 and M are constant, then

$$k_{24}[(CF_3)_2C{:}CF_2] + k_{44}[M]^2 = k_{43}[CF_3][(CF_3)_2C{:}CF_2] \quad . \; . \; . \; . \quad (46)$$

$$k_{42}[(CF_3)_2C{:}CF_2] + k_{43}[CF_3][(CF_3)_2C{:}CF_2] = k_{44}[M]^2 + k_{45}[M]^2 \quad . \; . \; . \quad (47)$$

whence

$$2k_{42}[(CF_3)_2C{:}CF_2] = k_{45}[M]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (48)$$

Assuming that the reaction chain length is long, we can show that,

$$-d[(CF_3)_2C{:}CF_2]/dt = 2(k_{42}k_{44}/k_{45})[(CF_3)_2C{:}CF_2] \quad . \; . \; . \; . \; . \; . \quad (49)$$

Using the integrated form of this equation we obtained the following values of $2k_{42}k_{44}/k_{45}$: at 700°, 37 sec.$^{-1}$; at 725°, 104 sec.$^{-1}$; at 750°, 307 sec.$^{-1}$. The ratio can be expressed as $1{\cdot}1 \times 10^{14} \exp(-82{,}700/RT)$ sec.$^{-1}$. This means that the activation energy for the initial split of perfluoro*iso*butene is not greater than 83 kcal. A similar conclusion is reached when some alternative reaction mechanisms are considered.

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