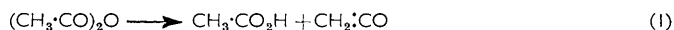


604. *The Thermal Decomposition of Perfluoroacetic Anhydride.*

By P. J. CORBETT and E. WHITTLE.

The thermal decomposition of perfluoroacetic anhydride has been studied in the range 216—320°. Below 260°, the products are almost entirely carbon monoxide, carbon dioxide, and trifluoroacetyl fluoride. These products are explained by means of a mechanism with the initial step $(\text{CF}_3\cdot\text{CO})_2\text{O} \longrightarrow \text{CF}_3\cdot\text{COF} + \cdot\text{CF}_2\cdot\text{CO}_2$. The biradical polymerises on the walls, and the polymer decomposes heterogeneously, giving carbon monoxide and dioxide as the only volatile products. At 320°, the pyrolysis of the anhydride gives the additional products, tetrafluoroethylene and polytetrafluoroethylene.

THERMAL decomposition of perfluoroacetic anhydride in the vapour phase is of interest because of its possible resemblance to the thermal decomposition of acetic anhydride. This has been studied by Murawski and Szwarc¹ who found that the reaction is homogeneous and involves the simple molecular reaction



If the analogous reaction occurred with perfluoroacetic anhydride, one of the products would be difluoroketen about which little is known. Alternatively, the decomposition could give rise to trifluoromethyl radicals, which would be useful as there are few convenient sources of this radical.

¹ Murawski and Szwarc, *Trans. Faraday Soc.*, 1951, **47**, 269.

We find however that the decomposition involves neither of these processes and has unusual complications.

EXPERIMENTAL

Materials.—Perfluoroacetic anhydride was made by the method of Bourne and his co-workers.² The product was fractionated and had b. p. 39° (lit., 39°). It was subjected to bulb-to-bulb distillations on the high-vacuum system and a middle cut was retained and stored at -80°.

Trifluoroacetyl fluoride was made by the method of Oláh, Kuhn, and Beke.³ It contained silicon tetrafluoride and trifluoroacetyl chloride as impurities. Silicon tetrafluoride was removed by passing the mixture through Carbosorb which has been degassed for 12 hr. at 60°. Trifluoroacetyl chloride was removed by low-temperature distillation.

Apparatus.—The reaction vessel was attached to a conventional high-vacuum system and was heated in an oven which was thermostat-controlled to $\pm 1^\circ$. The temperature variation along the vessel was less than 2°. Two cylindrical reaction vessels were used. One, made of stainless steel, was 15 cm. long and of 3.5 cm. internal diameter and had a volume of 170.4 ml.; the other was made of Pyrex glass and was 16 cm. long and of 3.7 cm. internal diameter with a volume of 189.4 ml. Either vessel was connected by means of a narrow capillary tube to a Springham greaseless tap immediately outside the oven.

Procedure.—Perfluoroacetic anhydride was thoroughly degassed and its vapour was then admitted to the reaction vessel. Subsequent changes in pressure were observed, if required, on a constant-volume mercury manometer. After a suitable time, the contents of the vessel were opened to a small trap cooled in liquid air, and the non-condensable portion was measured by means of a combined Toepler pump-gas burette. The gas burnt completely on copper oxide at 320° and consisted only of carbon monoxide. The residue in the trap was warmed to -80° and a second fraction was removed by means of the Toepler pump. Infrared analysis showed that this gas consisted of carbon dioxide and trifluoroacetyl fluoride, with traces of silicon tetrafluoride and tetrafluoroethylene. The mixture was analysed quantitatively, by exposing it for a short time to Carbosorb which removed only carbon dioxide, and treating the residue with water which left only tetrafluoroethylene. The amounts of silicon tetrafluoride and trifluoroacetyl fluoride were determined by infrared analysis.

The residue (from the reaction vessel) which was not volatile at -80° consisted only of perfluoroacetic anhydride, so that the fraction of anhydride decomposed could be measured, although with limited accuracy as the percentage decomposition was not usually large.

RESULTS AND DISCUSSION

Some typical results are shown in Table 1. The major products were carbon monoxide, carbon dioxide, and trifluoroacetyl fluoride. In all runs, approximately equal amounts of carbon monoxide and carbon dioxide were formed and the amount of trifluoroacetyl

TABLE 1.
The products of the pyrolysis of perfluoroacetic anhydride (stage 1).

Run	Temp.	P_0 (A) (mm.)	Time (min.)	(A) reacted		Products (10^5 mole)			
				10^5 mole	%	CO	CO ₂	CF ₃ ·COF	SiF ₄
P1	240°	120	228	12	17	4.53	5.78	14.7	0.00
P2	217	192	100	9	7.6	1.84	2.16	9.6	0.35
P3	216	123	100	7	9.2	1.50	1.57	8.4	0.69
S1	260	133	13.5	40	59	5.29	5.02	44.7	0.10
S2	256	127	13	31	47	2.50	2.44	33.4	0.10
S3	258	128	12	21	32	2.92	1.66	21.3	0.00

(A) = anhydride; P = Pyrex vessel; S = stainless-steel vessel.

fluoride produced was approximately equal to that of the anhydride decomposed. Changing from a Pyrex to a stainless-steel reaction vessel had little effect. However, the

² Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976.

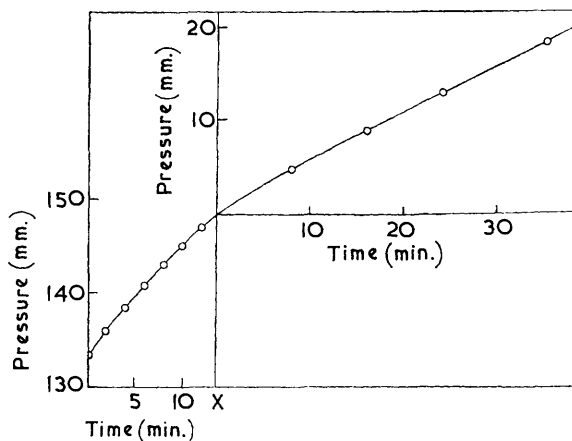
³ Oláh, Kuhn, and Beke, *Chem. Ber.*, 1956, **89**, 862.

composition of the product mixture varied with the time of decomposition: the longer the time of decomposition, the greater were the yields of carbon monoxide and dioxide relative to trifluoroacetyl fluoride although the last was always formed in largest amount. It appears that carbon monoxide and dioxide are formed at equal rates which are different to the rate of formation of trifluoroacetyl fluoride. This was confirmed by the following remarkable behaviour of the system.

The pressure in the reaction vessel was measured during a given run at regular intervals and after a suitable time the vessel was pumped to a good vacuum for a few minutes. It was then isolated, whereupon a steady pressure increase was observed; this behaviour is shown in the Figure. It is most striking that the pressure-time curve after pumping

Pressure changes during the pyrolysis of perfluoroacetic anhydride.

At X, reaction vessel was pumped for 13.5 min., then isolated.



is almost a continuation of the pressure-time curve before pumping. Let us denote the reactions before and after pumping by stage 1 and stage 2, respectively. Some typical analyses of the products of stage 2 are given in Table 2. The only major products are carbon monoxide and dioxide and again they are formed in approximately equal amounts.

TABLE 2.
The products of the pyrolysis of perfluoroacetic anhydride (stage 2).

Run	Temp.	Stage 1, time (min.)	Pumping time (min.)	Stage 2, time (hr.)	Final stage 2, pressure (mm.)	Products (10^5 mole)		
						CO	CO ₂	SiF ₄
S1	260°	13.5	13.5	20	93.8	21.1	25.5	0.21
S2	256	13	4	24	80.9	21.2	22.6	1.18
S3	258	12	3	66	66.4	17.9	19.3	1.45

See Table 1 for full details of stage 1.

Clearly the products of stage 2 must be formed by decomposition of involatile material on the surface of the reaction vessel and this must have been deposited during stage 1. We further conclude that the carbon monoxide and dioxide are produced in the same way in both stages since the pressure-time curve does not change very much from stage 1 to stage 2; this implies that any other reactions occurring do not involve a pressure change, *e.g.*, the initial step which leads to the deposit on the wall. We shall call this deposit "the polymer."

With some runs, there was an apparent induction period in that no pressure change occurred for the first few minutes. However, decomposition had occurred, giving several mm. of trifluoroacetyl fluoride but only traces of carbon monoxide and dioxide. This supports the idea that the initial reaction involves no pressure change.

If the results of Tables 1 and 2 are combined, the overall product yields shown in Table

3 are obtained. Apparently one molecule of trifluoroacetyl fluoride is formed per molecule of anhydride decomposed and the remaining two fluorine atoms are unaccounted for.

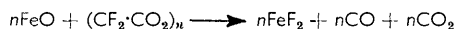
TABLE 3.
Total products (10^6 mole) of the pyrolysis of perfluoroacetic anhydride
(stage 1 + stage 2).

Run	Anhydride reacted	CO	CO ₂	CF ₃ ·COF	SiF ₄
S1	40	26.4	30.5	44.7	0.31
S2	31	23.7	25.0	33.4	1.28
S3	21	20.2	21.0	21.2	1.45

The above observations may largely be explained as follows. We postulate for the initial step

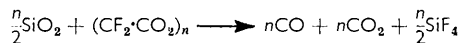


If the biradical (I) quickly polymerises on the walls, the overall process gives no pressure change, as suggested above. The polymer quickly begins to decompose, giving carbon monoxide and dioxide both in stage 1 and stage 2. In stage 2, however, all anhydride has been removed, so the decomposition of the polymer is the only reaction occurring. We were unable to obtain samples of the polymer but presumably its formula is $(\text{CF}_2 \cdot \text{CO}_2)_n$. Only a tentative explanation can be offered why its break-down yields only carbon monoxide and dioxide in equal quantities. If some oxide (iron or chromium, for example) is present in the steel vessel then a possible reaction is



If the metal itself reacts, rather than the oxide, then equal amounts of carbon monoxide and dioxide can be obtained only if carbon is deposited. After the work was completed, the steel vessel was cut open but no deposit or corrosion was observed.

In the glass vessel an obvious possible reaction is



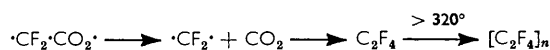
However, the yields of silicon tetrafluoride were much less than half those of carbon monoxide or dioxide, so that the fluorine atoms must react with and stay on the glass. At the end of the experiments the glass vessel appeared largely unchanged although there was a little etching at the end where the capillary joined it.

A series of experiments was done to measure the initial rate of pressure increase as a function of initial anhydride pressure in order to find the kinetic order of the reaction. For a given initial pressure and temperature, the initial rate was approximately the same in both steel and glass reaction vessels. In the glass vessel the order was 0.25 at 216° and 0.41 at 268° with a pressure range of 24—176 mm.; in the steel vessel the order was 0.56 at 258° with a range of 11—192 mm. These fractional orders refer, of course, to the process measured by dp/dt at zero time and we have suggested above that this process is the decomposition of the polymer. The fractional orders might be discussed in terms of the Langmuir theory, but there is the complication that the rate of the actual initial step, namely, decomposition of the anhydride, was not measured. Our results do not indicate whether the initial reaction is heterogeneous or homogeneous, so that further speculation is hardly justified.

Initial rates of pressure increase were measured at various temperatures, for the same initial pressures, and these led to activation energies, for the reaction causing the pressure increase, of 34 kcal. mole⁻¹ in the glass vessel and 39 kcal. mole⁻¹ in the steel vessel. On the basis of the mechanism proposed, these activation energies refer to decomposition of the polymer which is thus little affected by the nature of the surface.

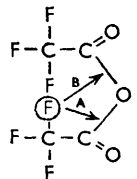
In a few experiments, pressure-time curves were obtained for the stage 2 reaction. In a typical experiment, a final pressure of 88 mm. was reached 21 hr. after the anhydride had been pumped away and this pressure was taken to be a measure of the polymer initially present. The fraction of polymer present at intermediate times could then be found from the appropriate pressure readings and the results accurately fitted a first-order plot. Hence the rate of decomposition of the polymer is proportional to the amount present.

In some experiments, traces of tetrafluoroethylene were found and in flow experiments at 320° appreciable amounts of polytetrafluoroethylene were formed. This is expected if the radical (I) decomposes thus:



The fact that no hexafluoroethane and little silicon tetrafluoride were formed suggests that no CF_3 radicals were formed since these radicals would probably dimerise or react with glass to give silicon tetrafluoride.⁴ No carbonyl fluoride was detected in the products although Dresdner, Mao, and Young⁵ have suggested that it is always formed when organic oxy-fluorine compounds are pyrolysed.

The pyrolyses of perfluoroacetic anhydride and acetic anhydride follow quite different patterns but the initial steps postulated are rather similar. If the encircled fluorine atom shown in the formula migrates along A with rupture of the C-O bond indicated, the products would be $\text{CF}_3\cdot\text{CO}_2\text{F}$ and $\text{CF}_2\cdot\text{CO}$ which is exactly analogous to what happens with acetic anhydride [see reaction (1)]. However, if path B is followed, the products are just what we postulate in reaction (2).



It is of interest to compare the present work with the pyrolysis of hexafluoroacetone studied by Batey and Trenwith.⁶ The initial step proposed was



which involves migration of a fluorine atom to give trifluoroacetyl fluoride and a biradical as in reaction (2). The authors concluded that no CF_3 radicals were formed. They also studied the pyrolysis of carbonyl fluoride, and the products were found to be carbon monoxide and a little silicon tetrafluoride. The missing fluorine atoms presumably reacted with the steel reaction vessel used, as we have postulated for stage 2 of the decomposition of the anhydride.

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⁴ Ayscough and Steacie, *Proc. Roy. Soc.*, 1956, *A*, **234**, 476.

⁵ Dresdner, Mao, and Young, *J. Org. Chem.*, 1959, **24**, 698.

⁶ Batey and Trenwith, *J.*, 1961, 1388.