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OXIDATION REACTIONS OF TETRAFLUOROETHYLENE AND PRODUCTS THEREFROM—II

PHOTOCHEMICAL REACTIONS*

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Abstract—The influence of the concentration of oxygen without any added photosensitizing agent on the photolysis of gaseous tetrafluoroethylene has been studied at 2537 Å and 1849 Å. The results are discussed in relation to the different products obtained and their possible mechanism of formation.

THE Hg-sensitized photolysis of tetrafluoroethylene with UV light of 2537 Å was first studied by Atkinson[1] and reported to give mainly perfluorocyclopropane and polytetrafluoroethylene. While this work was in progress, a few publications dealing with the radiation-induced oxidation of tetrafluoroethylene have appeared. This was accomplished by high-energy radiations[2] or by UV light in the presence of photoinitiators such as halogens[3] or mercury.[4,5] In the case of mercury, the 2537 Å line was used and the oxidation investigated with either molecular[4] or atomic oxygen,[5]

The present work was carried out using a low-pressure Hg-lamp, with an output of 13·8 Watts at 2537 Å and a minor amount of energy at 1849 Å.† No photosensitizers or initiators were added, unless otherwise specified.

RESULTS

In the first instance, the influence of oxygen, in amounts varying from few ppm to 50%, on the photolysis of tetrafluoroethylene was studied. The reaction was carried out at ca. 800 mm Hg using UV light filtered through an 8 mm layer of either water or acetic acid. The lamp, as shown in Fig. 1, was coaxial with a cylindrical jacket, made of fused quartz, in which the filter liquid was made to circulate at the controlled temperature of 30°. The jacket fitted by a ground-glass joint into a larger Pyrex container, the actual reactor, which was connected with conventional vacuum equipment and a sulphuric acid pressure gauge. The results are given in Table 1.‡

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† Although the intensity of the 1849 Å line was different for different lamps of the same stock, it was estimated to be around $4 \cdot 10^{-3}$ einstein/hr as determined by nitrous oxide actinometry.[6]

‡ Runs No. 1 and 10 were carried out in the presence of Hg for comparison purposes.

[1] B. Atkinson, *J. Chem. Soc.* 2684 (1952).

[2] [a] V. Caglioti, M. Lenzi and A. Mele, *Nature, Lond.* **201**, 610 (1964); [b] D. Cordischi, M. Lenzi and A. Mele, *Trans. Faraday Soc.* **60**, 2047 (1964); [c] V. Caglioti, A. Delle Site, M. Lenzi and A. Mele *J. Chem. Soc.* 5430 (1964).

[3] H. H. Gibbs and J. L. Warnell, Fr. Pat. 1.322.597 (Feb. 18, 1963 to E. I. DuPont de Nem.).

[4] J. Heicklen, V. Knight and S. A. Greene, *J. Chem. Phys.* **42**, 221 (1965).

[5] D. Saunders and J. Heicklen, *J. Amer. Chem. Soc.* **87**, 2088 (1965).

[6] F. Gozzo and V. Oprandi, unpublished results.

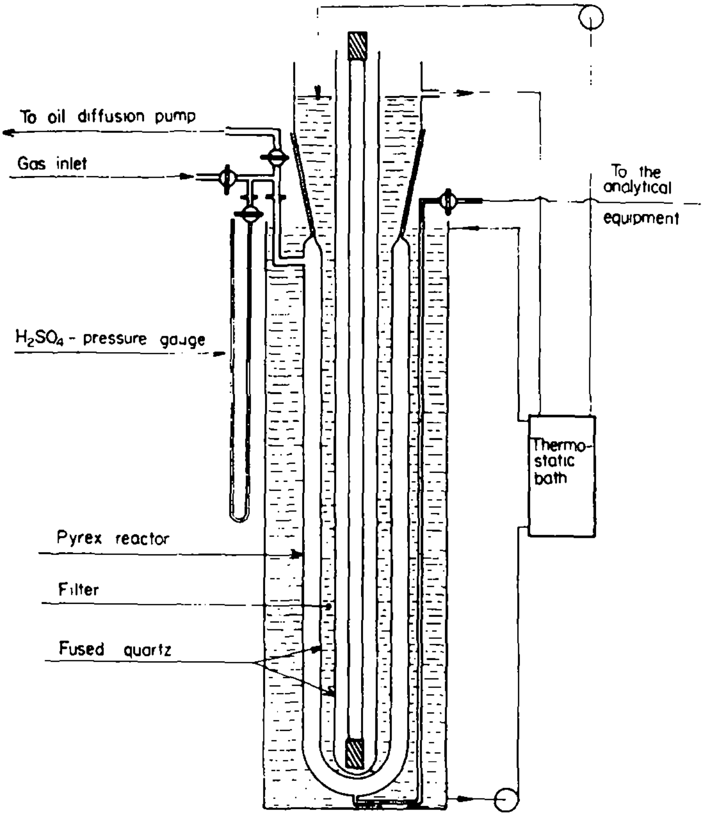

Fig. 1. Reactor for the experiments with filtered light.

Concentrations of oxygen up to about 20 ppm appeared to initiate the photopolymerization of tetrafluoroethylene. Polytetrafluoroethylene was the main product of the reaction together with minor amounts of perfluorocyclopropane. Although the results were somewhat scattered, the same trend was found using either 3M aqueous AcOH ($\lambda > 2440$ Å; transmittance at 2537 Å = ca. 60%) or distilled water ($\lambda > 1850$ Å; transmittance at 2537 Å = ca. 100%) as filters.

At higher concentrations, oxygen appeared to inhibit polymerization and only small amounts of tetrafluoroethylene oxide, carbonyl fluoride and perfluorocyclopropane were found. The amounts of perfluorocyclopropane were not markedly affected by the concentration of oxygen.

A similar set of experiments was then carried out with the UV lamp directly immersed in the gas. Since C_2F_4 is known to give a continuous absorption below 2150 Å,[7] it can be assumed that most of the 1849 Å line was strongly absorbed by the olefin. Under these conditions the temperature of the gas could not be kept at a fixed value and was estimated to be in the range between 50° and 60°. Total pressure was always approximately 800 mm Hg. When the concentration of O_2 was a few ppm the rate of pressure decrease was constant and reproducible, and polytetrafluoroethylene and perfluorocyclopropane were formed. In the presence of higher concentrations of oxygen (few units % or more) formation of polytetrafluoroethylene

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[7] J. R. Lacher, L. E. Hammel, E. F. Bohnfalk and J. D. Park, *J. Amer. Chem. Soc.* **72**, 5486 (1950).

TABLE 1. EXPERIMENTS WITH FILTERED LIGHT (total initial press = 760–820 mm Hg)

Run No.	Filter	O_2 conc	Hg	Total irradiation time	$100 \frac{\Delta P}{P}$ (after 2^h)	$100 \frac{\Delta P}{P}$ (final)	Final molar conversion % of C_2F_4 into c-C_3F_6	$(CF_2)_n$	COF_2	C_2F_4O
1	3M AcOHaq	*	pres.	2 hr	21	21	8·5	18·3	—	—
2	id	*	—	2 hr 40 min	—	—	0·1	—	—	—
3	id	2 ppm	—	3 hr	0·9	2	0·5	1·8	—	—
4	id	5 ppm	—	2 hr	4·1	4·1	0·4	4	—	—
5	id	9 ppm	—	2 hr 30 min	6·4	8·7	0·5	8·5	—	—
6	id	16 ppm	—	2 hr 18 min	10·4	12·3	0·3	12	tr	—
7	id	50 ppm	—	3 hr	2·1	3·9	n.c.	3·8	27 ppm	—
8	id	500 ppm	—	3 hr	0·5	0·8	0·3	0·7	0·01	tr
9	id	50%	—	3 hr	—	—	0·1	—	0·1	0·1
10	id	50%	pres.	2 hr	9·8	9·8	3·3	—	13·3	19·2
11	H_2O	*	—	4 hr		1·2	0·8	0·9	—	—
12	id	2 ppm	—	2 hr	2·4	2·4	0·1	2·4	—	—
13	id	4 ppm	—	3 hr	4·4	8·1	0·6	7·9	—	—
14	id	15 ppm	—	1 hr 30 min	10·4	7·5	0·7	7·2	—	—
15	id	34 ppm	—	4 hr 30 min	2·4	7·3	0·3	7·2	30 ppm	—
16	id	85 ppm	—	3 hr	2	3·3	0·1	3·2	80 ppm	tr
17	id	150 ppm	—	4 hr	2	6·6	0·5	6·4	0·01	tr
18	id	590 ppm	—	2 hr 5 min	1·5	1·6	0·1	1·5	0·02	0·03
19	id	5%	—	4 hr	—	—	0·1	—	0·2	0·2
20	id	50%	—	3 hr	—	—	0·2	—	0·2	0·2

* Below the analytical limits (ca. 2 ppm).

was inhibited until most of the oxygen had been consumed. At this point (see curve ⊗ in Fig. 2) auto-acceleration was observed together with the homopolymerization of the olefin. The results of some runs are shown in Table 2. Until the formation of polytetrafluoroethylene was inhibited, the main products were tetrafluoroethylene oxide and carbonyl fluoride, together with minor amounts of perfluorocyclopropane, the formation rate of which was apparently unaffected by oxygen concentration. At the same time small amounts of a high boiling liquid were obtained, the molecular formula of which was CF_2O. Although its C:F:O ratio was the same as that of the copolymer obtained by auto-oxidation,[8] the former contained only very small amounts of peroxidic oxygen (about 1% of the total oxygen). It was partly decomposed by water or strong acidic solutions with formation of carbon dioxide and hydrogen fluoride. The IR spectrum of the residue showed a weak absorption in the region of carboxylic groups. On treatment with strong organic bases an even smaller residue was obtained, the IR spectrum of which was identical with that of the starting material and the first residue but did not display any band in the carboxylic group

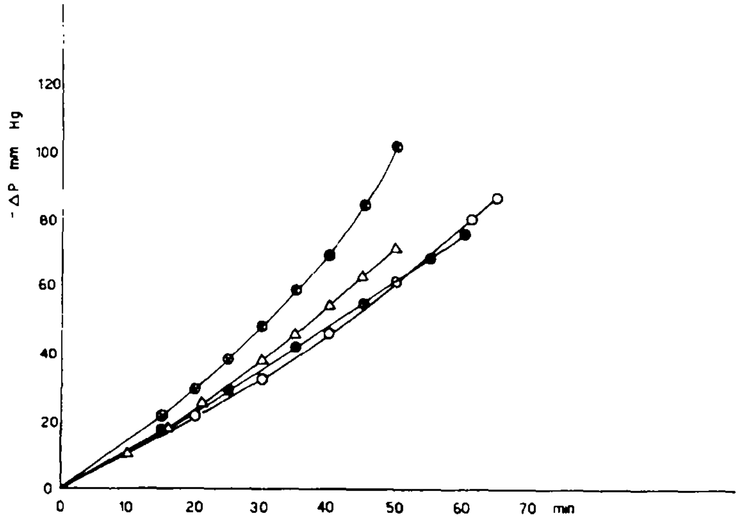

Fig. 2. Experiments with direct light in static phase:
● O_2 = 2 ppm; ○ O_2 = 0·13%; ⊗ O_2 = 9%; △ O_2 = 50%.

TABLE 2. EXPERIMENTS WITH DIRECT LIGHT IN STATIC PHASE
(Total initial press = 800–830 mm Hg)

Run No.	O_2 conc	Irradiation time (min)	$100\frac{\Delta P}{P}$	Final molar conversion % of C_2F_4 into				
				c-C_3F_6	$(CF_2)_n$	COF_2	C_2F_4O	$(CF_2—O)_n$
1	4 ppm	50′	8·8	1·7	8·3			
2	2 ppm	60′	9·4	1·8	8·9			
3	0·13%	65′	10·4	1·8	10·2	tr	tr	—
4	9·2%	50′	12·6	1·5	6	3·4	8·1	tr
5	51·4%	50′	8·9	2·0	—	10·7	20·9	3·3

Volume of the reactor = 760 ml; diameter = 36 mm.

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[8] F. Gozzo and G. Camaggi, *Tetrahedron* **22**, 1765 (1966).

region. The NMR spectrum of both the starting material and the residue showed a main signal at −21·9 ppm with respect to trifluoroacetic acid.* Both the position of the signal and the results of chemical characterization are consistent with a poly(oxydifluoromethylene) structure.

Other experiments were carried out in a bigger reactor. Results in Table 3 indicate that the reaction between tetrafluoroethylene and oxygen is slightly autoaccelerated even at high concentrations of the latter. Quantum yields have been estimated to be near to two by extrapolation at low conversions.[6] When the reaction was carried out with an oxygen-tetrafluoroethylene molar ratio slightly greater than one, comparatively larger amounts of carbonyl fluoride were formed. Accordingly, if the irradiation was prolonged till after all tetrafluoroethylene had been consumed (run No. 9) tetrafluoroethylene oxide was further oxidized to give carbonyl fluoride with minor amounts of perfluorodimethyl peroxide and perfluorodimethyl ether. In fact the same set of products was obtained by irradiation of mixtures of tetrafluoroethylene oxide and oxygen, whereas irradiation of tetrafluoroethylene oxide alone gave carbonyl fluoride, perfluoroethane, perfluoropropane, trifluoroacetyl fluoride and minor amounts of other compounds.

TABLE 3. EXPERIMENTS WITH DIRECT LIGHT IN STATIC PHASE

	p (mm. Hg)			Amounts of C_2F_4 (mmoles) converted into					
Run No.	C_2F_4	O_2	Time	CF_3OOCF_3	CF_3OCF_3	C_2F_4O	COF_2	c-C_3F_6	CF_2O_n
1	401	202	15 min	—	—	1·1	0·6	0·15	not calctd.
2	401	202	30 min	—	—	2·6	1·45	0·42	not calctd.
3	403	202	1 hr	—	—	6·2	3·15	0·90	not calctd.
4	401	203	2 hr	—	—	13·6	7·25	1·57	not calctd.
5	373	409	1 hr	—	—	4·9	3·8	1	1–2
6	373	409	2 hr	—	—	11·6	8·6	2·5	2–3
7	373	409	4 hr	—	—	30·3	20·3	5	6–7
8	373	409	7 hr	tr.	—	52·3	48·7	10·5	14·0
9	373	409	14 hr	0·6		26·8	75·1	9·8	14·0

Volume of the reactor = 5000 ml; diameter = 85 mm.

The photolysis of tetrafluoroethylene, with or without oxygen, was studied also in the presence of a large excess of nitrous oxide and the results are given in Table 4. It is of interest that the ratio between the amounts of perfluorocyclopropane (referred to PC_2F_4 = 55 mm Hg) and nitrogen formed, is not significantly lowered on addition of molecular oxygen.

A different series of experiments was carried out by a flow method. The flow rate of tetrafluoroethylene was kept constant at certain values (37·5 and 18·7 mmoles/hr) while that of oxygen was varied in correspondence with a partial pressure between 2 and 600 mm of Hg, the atmospheric pressure difference being made up by nitrogen. The reactor was of the type used for the static experiments. The gases flowing out

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* Calculated by using hexafluorobenzene as the reference standard.

of the reactor were analysed by GLC. The results of a few runs are shown in Table 5. When the partial pressure was low, oxygen was nearly completely consumed to give tetrafluoroethylene oxide and carbonyl fluoride as the primary products of the reaction in a 1 : 1 molar ratio. The formation of polytetrafluoroethylene was inhibited for a oxygen : tetrafluoroethylene molar ratio greater than 1 : 6 while poly(oxydifluoromethylene) was formed. The rates of formation of both the latter and the oxygen-containing volatile products rose to a maximum for a tetrafluoroethylene : oxygen molar ratio of approx 2 (at a partial pressure of tetrafluoroethylene = 228 mm Hg). Under these conditions the ratio between the amounts of tetrafluoroethylene converted into poly(oxydifluoromethylene) and oxygen-containing volatile products was about 1 : 7. At higher oxygen concentrations the rate of formation of poly(oxydifluoromethylene) was constant, while that of tetrafluoroethylene oxide slowly decreased. A minor amount of perfluorocyclopropane was always among the products, its formation rate being not significantly affected by the concentration of oxygen. Experiments carried out with lower partial pressures of tetrafluoroethylene resulted in smaller amounts of tetrafluoroethylene oxide and perfluorocyclopropane being formed with respect to carbonyl fluoride and poly(oxydifluoromethylene).

TABLE 4. EXPERIMENTS IN THE PRESENCE OF N_2O

	p (mm Hg)			Time	mmoles of products				
Run No.	C_2F_4	O_2	N_2O	(min)	N_2	COF_2		$c\text{-}C_3F_6$	$\frac{55}{P_{C_2F_4}} \cdot \frac{c\text{-}C_3F_6}{N_2}$
1	56	—	443	15	0·71	0·7	tr	0·21	0·29
2	55	55	446	15	0·11	0·7	0·3	0·03	0·27
3	54	—	447	30	1·31	1·3	tr	0·44	0·34
4	56	23	448	30	0·23	1·5	0·36	0·07	0·30
5	45	52	454	30	0·30	1·3	0·4	0·05	0·20
6	52	101	455	30	0·23	1·4	0·5	0·06	0·28
7	59	—	447	60	1·90	1·9	tr	0·68	0·33
8	50	54	450	60	0·48	3·4	1·1	0·12	0·28

Volume of the reactor = 5000 ml. Diameter = 85 mm.

TABLE 5. EXPERIMENTS WITH DIRECT LIGHT IN A FLOW SYSTEM

	Flow rate mmoles/hr			O_2 partial press	mmoles/hr of C_2F_4 converted into				
Run No.	C_2F_4	O_2	N_2	mm Hg	C_2F_4O	COF_2	$c\text{-}C_3F_6$	$(CF_2O)_n$	$(CF_2)_n$
1	37·5	0·3	87·5	1·7	0·1	0·1	0·5	—	2·8
2	37·5	4·4	83·3	27	2·9	1·6	0·7	tr	1·6
3	37·5	11·7	75·8	71	6·3	3·2	0·8	1·2	—
4	37·5	17·5	70	106	6·3	3	0·6	1·4	—
5	37·5	37·5	50	225	5·7	3·7	0·5	1·4	—
6	37·5	65·8	21·7	400	5·6	3·4	0·5	1·5	—
7	37·5	87·5	—	530	5·3	3	0·6	1·3	—
8	18·7	87·5	18·7	530	3·1	2·9	0·3	1·4	—

DISCUSSION

The most remarkable feature of the experiments carried out with filtered light (λ = 2537 Å) which is not directly absorbed by tetrafluoroethylene is the pronounced accelerating effect of oxygen, in concentrations up to about 20 ppm, on the polymerization of tetrafluoroethylene. Higher concentrations of oxygen have an equally strong inhibiting effect on the polymerization. Under these conditions only small amounts of carbonyl fluoride tetrafluoroethylene oxide and perfluorocyclopropane are formed. The total conversion of tetrafluoroethylene to these products does not vary significantly with the concentration of oxygen.

The initiating process is rather obscure. Reactions between olefins and oxygen, initiated by light which is not apparently absorbed by the system, can be found in the literature.[9,10] In particular, it has been suggested that some olefins, e.g. monochlorotrifluoroethylene, may undergo a direct addition of molecular oxygen to the double bond,[10,11] followed by decomposition of the peroxidic bond.

In this work small amounts of perfluorocyclopropane were formed even in the absence of oxygen. This might be due to the action of the 2537 Å line on some residual sensitizing agent. Under these conditions, formation of polytetrafluoroethylene could not be noticed. The fact that polymerization occurred with traces of oxygen strongly suggests that the latter promotes the formation of very active initiating agents. It is of interest that, with high concentrations of oxygen, no oxygen-containing polymers are formed. The growth of peroxidic chains is probably hindered by their intrinsic instability and the only possible reactions are those leading to volatile products when homopolymerization of tetrafluoroethylene is inhibited. When the reaction is photosensitized by mercury and the oxygen concentration is high, a more than hundredfold increase is noticed in the reaction rate.

A different situation arises using light containing the 1849 Å line, which is directly absorbed by both tetrafluoroethylene[7] and oxygen[12] but mainly by the former when their concentrations are comparable. Although the interpretation of the experimental results is by no means straight-forward, it is possible to draw some conclusions. It is unlikely that carbonyl fluoride and tetrafluoroethylene oxide are formed by a mechanism involving the reaction of difluorocarbene with molecular oxygen such as:

$$C_2F_4 \xrightarrow{h\nu} 2CF_2 \tag{1}$$

$$CF_2 + O_2 \longrightarrow COF_2 + O \tag{2}$$

$$O + C_2F_4 \longrightarrow C_2F_4O \tag{3}$$

or

$$CF_2 + O_2 \longrightarrow CF_2O_2 \tag{4}$$

$$CF_2O_2 + C_2F_4 \longrightarrow COF_2 + C_2F_4O \tag{5}$$

In fact difluorocarbene, as obtained by either Hg-sensitized[4] or direct[13] photolysis of tetrafluoroethylene, or by photolysis of both bromodifluoro- and dibromodifluoromethane,[14] has been reported to be unreactive towards molecular oxygen. These

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[9] E. H. Farmer and A. Sundralingham, *J. Chem. Soc.* 121 (1942).

[10] R. N. Haszeldine and F. Nyman, *J. Chem. Soc.* 1084 (1959).

[11] G. A. Russel, *Peroxide reaction mechanism* p. 112 (Edited by J. O. Edwards) p. 112. Interscience, (1962).

[12] E. Briner, *Ozone chemistry and technology*, p. 1 (Edited by ACS) p. 1. Appl. Publ., Washington (1959); see also R. Nagy, *Idem.* p. 57.

[13] F. W. Dalby, *J. Chem. Phys.* **41**, 2297 (1964).

[14] J. P. Simons and A. J. Yarwood, *Nature, Lond.* **192**, 943 (1961).

findings are confirmed in the present work, since the rate of formation of perfluorocyclopropane in the direct photolysis of tetrafluorethylene is not significantly lowered by high concentrations of oxygen. Furthermore reaction (3) should be ruled out in view of the results of the photolysis of tetrafluoroethylene in the presence of a large excess of nitrous oxide (cf. Table 4). These show that in the absence of molecular oxygen no epoxide is formed and that carbonyl fluoride and nitrogen are obtained in a 1:1 molar ratio, and thus they are consistent with a mechanism involving reactions (6) and (7)

$$N_2O \xrightarrow{h\nu} N_2 + O \tag{6}$$

$$O + C_2F_4 \longrightarrow COF_2 + CF_2 \tag{7}$$

A similar scheme[5] to explain the results of the Hg-sensitized photolysis of mixtures of the same two gases has been suggested by other workers.[5] In this work addition of oxygen sharply reduces the amount of both perfluorocyclopropane and nitrogen formed, their ratio remaining practically constant. At the same time substantial amounts of tetrafluoroethylene oxide are produced, while there is no significant increase in the formation of carbonyl fluoride. Molecular oxygen would thus appear to partially inhibit reaction (6), but to have little influence on the total conversion of tetrafluoroethylene. A different mechanism should be operating in this case. Perhaps the formation of both tetrafluoroethylene oxide and most of the carbonyl fluoride is brought about by some oxidizing species that may be continuously produced through absorption of light. The results also indicate that the difluorocarbene responsible for the formation of perfluorocyclopropane displays very little reactivity towards molecular oxygen.

Thus all the experimental evidence suggests that reaction (1) may not be the primary step in the photo-oxidation of tetrafluoroethylene. In fact difluorocarbene may well be formed by a different route, as shown by the presence of perfluorocyclopropane among the volatile products of the auto-oxidation of tetrafluoroethylene in the dark.[8] An alternative mechanism which would accomodate the available experimental evidence might involve an excited state of tetrafluoroethylene, formed on absorption of light, which would then react with oxygen according to either (9) or (11):

$$C_2F_4 \xrightarrow{h\nu} C_2F_4{}^* \tag{8}$$

$$C_2F_4{}^* + O_2 \longrightarrow CF_2 + \cdot CF_2OO\cdot \tag{9}$$

$$\cdot CF_2OO\cdot + C_2F_4 \longrightarrow COF_2 + C_2F_4O \tag{10}$$

$$C_2F_4{}^* + O_2 \longrightarrow \cdot C_2F_4OO\cdot \tag{11}$$

$$\cdot C_2F_4OO\cdot + C_2F_4 \longrightarrow C_2F_4O + COF_2 + CF_2 \tag{12}$$

Carbonyl fluoride and tetrafluoroethylene oxide are in fact formed in a molar ratio which is near to one in most of the experiments and greater than one only when an excess of oxygen is used in the static phase. This is in fair agreement with the proposed mechanism, considering that tetrafluoroethylene oxide can be further photo-oxidized mainly to carbonyl fluoride. Reactions (8) to (12) are also consistent with the extrapolated quantum yield at low conversions (ca. 2). However, the actual formation of activated tetrafluoroethylene has not been proved. Also, it is difficult to discriminate the two possible reaction pathways, i.e. (9)–(10) or (11)–(12), though it might be argued that (12) would conceivably produce triplet difluorocarbene which should then react with oxygen according to (2) or (4). Thus the alternative pathways, (9)–(10), might be preferred. Reaction (11) would be of importance in the auto-oxidation of tetrafluoroethylene in the dark,[8] although the initiation step of the reaction must be a matter of speculation.

Any attempt to account for the formation of poly(oxydifluoromethylene) requires a complicated set of reactions involving the cleavage of both carbon–carbon and oxygen–oxygen bonds. Since both trifluoromethyl and acyl fluoride are the end groups of this polymer it may be assumed that at least some of the chains are initiated by trifluoromethyl radicals produced by the decomposition of tetrafluoroethylene oxide via rearrangement to trifluoroacetyl fluoride:

$$C_2F_4O \xrightarrow[\text{or } \Delta]{h\nu} CF_3 - COF \xrightarrow{h\nu} CF_3\cdot + \cdot COF \qquad (13)$$

This hypothesis is supported by the presence of hexafluoroethane among the products of the photolysis of the epoxide in the absence of oxygen. The formation of the poly(oxydifluoromethylene) may be tentatively rationalized in terms of the following reactions, some of which have been postulated in the literature for the oxidation reaction of olefins containing reactive double bonds:

$$R\cdot + O_2 \longrightarrow R - O - O\cdot \qquad (14)$$

where $R\cdot = CF_3\cdot$ or, more generally, $\sim CF_2$.

$$R - O - O\cdot + C_2F_4 \rightarrow R - O\cdot + C_2F_4O \qquad (15)$$

$$R - O\cdot \begin{cases} + C_2F_4 \rightarrow R - O - CF_2 - CF_2\cdot & (16) \\ + C_2F_4O \rightarrow R - O - CF_2 - CF_2 - O\cdot & (16\text{ bis}) \end{cases}$$

$$R - O - CF_2 - CF_2\cdot + O_2 \rightarrow R - O - CF_2 - CF_2 - O - O. \qquad (17)$$

$$R - O - CF_2 - CF_2 - O - O\cdot + C_2F_4 \rightarrow R - O - CF_2 - CF_2 - O\cdot + C_2F_4O \qquad (18)$$

$$R - O - CF_2 - CF_2 - O\cdot \rightarrow R - O - CF_2\cdot + COF_2 \qquad (19)$$

$$R - O - CF_2\cdot + O_2 \rightarrow R - O - CF_2 - O - O\cdot \qquad (20)$$

Reaction (19) implies that cleavage of the chain to carbonyl fluoride occurs only at the carbon–carbon bond of an alkoxy radical. If the sequence of reactions (16) to (19) controls the growth of the chain, the minimum amount of tetrafluoroethylene converted into oxygen-containing volatile products should be five times as much as that converted into poly(oxydifluoromethylene). While this has been found to be the case in all the experiments reported in the present work, we have found that under different conditions the conversion into the polymer can be as high as one third of that into volatile products. This fact may be accounted for by a mechanism in which reaction (16 bis) is competing with reactions (16) to (18).

EXPERIMENTAL

The tetrafluoroethylene used in this work was prepared as described in Part I.[8] Much of the work, particularly the photochemical reaction with filtered light, was carried out after further purification of the olefin through molecular sieves. The product thus obtained did not contain any impurity which could be detected by GPC. When O_2-free tetrafluoroethylene was needed, the gas was passed over manganous oxide which reduced the O_2 concentration below 2 ppm.

Commercial-grade O_2, dried over P_2O_5 was used when substantial amounts of it were needed. If controlled small amounts (few ppm) of O_2 were added to tetrafluoroethylene, they were produced at a Pt anode by passing a direct current of known intensity through a $CuSO_4$ solution. Concentrations of O_2 below 100 ppm were determined electrochemically by a Hersch O_2 meter, made by Engelhard Ind. Ltd. Higher concentrations of both O_2 and N_2 were measured by GPC using column A (see below) together with a molecular sieve column when necessary. The gaseous products were analysed by GPC using two columns: (A) was 8 m long and 4 mm in diameter; stationary phase: bis(2-ethylhexyl)sebacate supported on Kieselghur and kept at $-9°$. (B) was 8 m long and 4 mm in diameter; stationary phase: γ-butyrolactone supported on Kieselghur and kept at 0°. In both columns He was used as the carrier gas. The areas of all the peaks except that of perfluorocyclopropane, were standardized using pure samples. CoF_2 was converted quantitatively into CO_2 on passage through either columns.

Tetrafluoroethylene oxide gave a peak on column A only. IR spectra were run on a Model 21 Perkin–Elmer spectrometer. NMR measurements were taken on a Model A56–60 Varian spectrometer.

Photochemical oxidation. In all the experiments carried out in static phase the course of the reaction was followed by the variation of the press as determined by a H_2SO_4 gauge in order to avoid contamination by Hg. Before each run the reactor was evacuated for a few hr by a high-vacuum, oil-diffusion pump. Then tetrafluoroethylene was introduced, with or without O_2, into the reactor through a vacuum line, provided with a H_2SO_4 relief valve. The volatile products were analysed and separated by GPC. All of them were characterized by IR and, if necessary, mass spectrometry.

The amounts of polytetrafluoroethylene formed were estimated by the pressure drop in the system together with the GPC analysis of the volatile products. Poly(oxydifluoromethylene) was determined by wt. For the experiments with nitrous oxide the commercial-grade, pure gas was first condensed into a trap cooled by liquid N_2, then freed from N_2 by trap-to-trap vacuum distillation. The products were analysed by GPC in the usual way.

All the experiments carried out by the flow method lasted several hr. The amounts of the volatile products are given as the average of all the GPC analyses which were made frequently during the runs. Poly(oxydifluoromethylene) was weighed at the end of each run.

Tetrafluoroethylene, O_2 and N_2 when needed, were mixed together in a tower packed with glass beads, then dried over P_2O_5 before entering the top of the reactor. Poly(oxydifluoromethylene) was collected into a small flask fitted to the bottom of the reactor by a ground-glass joint and provided with a side arm for the outlet of the gaseous products. These could be either analysed by GPC or condensed into a trap, cooled by trichlorofluoromethane kept at -110 $-120°$ with liquid N_2, *via* a 3-way tap. Explosions occurred sometimes when undiluted mixtures were used at high flow rates and apparently took place immediately upstream or downstream with respect to the reactor, as shown by the formation of charcoal.

Tetrafluoroethylene oxide. Tetrafluoroethylene oxide was irradiated by an UV lamp emitting a large amount of energy at 1849 Å. After ca. 20 hr irradiation the products were examined and separated by GPC (column A). About 50% of the starting material was recovered unchanged. The main products were found to be CO_2 and perfluoroethane. Minor amounts of perfluoropropane and perfluorocyclopropane were also present together with traces of unidentified products. The IR spectrum of the gaseous mixture showed bands which could be attributed to COF_2 and trifluoroacetyl fluoride. Oxalyl fluoride might also be present.

When the reaction was carried out in the presence of substantial amounts of O_2 (30–50%) the main products isolated by GPC were found (IR) to be CO_2, perfluorodimethyl ether and perfluorodimethyl peroxide.

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