

1035. Oxidation of Tetrafluoroethylene by Molecular Oxygen.

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The main products of the oxidation of tetrafluoroethylene induced by heat, ultraviolet light, and ionizing radiation are carbonyl fluoride, tetrafluoroethylene oxide, hexafluorocyclopropane, and a liquid polymeric peroxide. The reactions were carried out by a static method in the gas phase.

In an earlier Note,¹ it was shown that tetrafluoroethylene reacts with oxygen under γ - or X-irradiation.* The present Paper gives further results on the oxidation induced by ionizing radiation together with those obtained by subjecting tetrafluoroethylene and oxygen mixtures to thermal treatment or ultraviolet irradiation. The oxidation leads in all cases to carbonyl fluoride, tetrafluoroethylene oxide, hexafluorocyclopropane, and a polymeric-peroxidic liquid ($C_2F_4O_2$)_x. For all the irradiations, at room temperature, the products account for more than 90% of the gaseous mixture. On the other hand, a proportionately large yield of hexafluorocyclopropane is obtained in the thermal reaction. These results are summarized in Table I.

TABLE I.
Oxidation of 1 : 1 mixtures of tetrafluoroethylene and oxygen.

Compound	Initial pressure (mm. Hg)			
	760	650	760	760
	X-Rays 0.4 Mr/hr. 1.5 hr.	γ -Rays 0.4 Mr/hr. 1.5 hr.	u.v. light 24 hr.	100° 14 hr.
C ₂ F ₄	25.3	22.0	64.2	15.5
O ₂	18.3	15.7	43.0	8.5
COF ₂	47.2	47.5	47.4	41.7
C ₂ F ₄ O.....	37.2	30.1	40.0	14.7
(CF ₂) ₃	4.5	5.7	7.0	42.0

The tetrafluoroethylene and the oxygen consumed are referred to 100 moles of their initial values. The products are reported as percentage of tetrafluoroethylene consumed which is found in the indicated product.

The effect of temperature on the γ -ray-induced reaction is shown in Table 2. The ratio between carbonyl fluoride and tetrafluoroethylene oxide remains practically constant. The yield of hexafluorocyclopropane decreases slightly as the temperature falls.

* Since the submission of this Paper, a patent from du Pont de Nemours (Fr. Pat. 1,322,597/1963; *Chem. Abs.*, 1963, 59, 11423) has described the halogen-sensitized photochemical oxidation of tetrafluoroethylene.

¹ V. Caglioti, M. Lenzi, and A. Mele, *Nature*, 1964, 201, 610.

TABLE 2.

Oxidation of 1 : 1 mixtures of tetrafluoroethylene and oxygen by γ -rays. Pressure, 650 mm. Hg; dose-rate 0.40 Mr/hr.; dose: 0.40 Mr.							
Compound	-25°	0°	+25°	Compound	-25°	0°	+25°
C ₂ F ₄	9.5	11.7	14.4	COF ₂	18.2	31.2	47.7
O ₂	4.5	7.1	10.3	(CF ₂) ₂ O	10.5	19.4	30.1
				(CF ₂) ₃	1.6	3.4	5.7
				Balance	67.9	42.9	11.8

See footnote to Table 1.

A peroxidic intermediate has been generally suggested for this type of reaction.²⁻⁵ However the structure of these compounds and the role they play in the formation of the various products are controversial.

Myers,² and Haszeldine and Nyman,³ studying the oxidation of chlorotrifluoroethylene, postulated cyclic peroxides as intermediates; Ambros⁴ obtained a polymeric peroxide. A polymeric peroxide was also postulated by Mayo⁵ for the oxidation of various vinyl compounds, and he put forward a kinetic scheme consistent with its formation. The polyperoxide found in the oxidation of tetrafluoroethylene is in agreement with this hypothesis (see D. Cordischi, M. Lenzi, and A. Mele, *Trans. Faraday Soc.*, in the press).

EXPERIMENTAL

Materials.—Tetrafluoroethylene was prepared as previously described.⁶ "Pure" (99.9%) oxygen was obtained commercially.

Radiation Source.—A 600-c ⁶⁰Co irradiating unit and a 50 kv X-ray apparatus were the radiation sources. Dose-rate was measured by the Fricke dosimeter [G(Fe³⁺) 15.68].⁶ A 75-w low-pressure mercury lamp was used for the photochemical reactions.

Apparatus.—Conventional gas-chromatographic equipment was used. The detector was a gas conductivity cell with thermistors, and the column 10 m. in length packed with 30—60 mesh Celite with 20% of perfluorotributylamine or 20% "kel-F-3" oil. Hydrogen was used as carrier gas at a flow rate of 6 l/hr. Column and detector were kept at -10°.

A Perkin-Elmer 237G double-beam infrared spectrophotometer was used with 8 cm. cells fitted with sodium chloride windows.

Molecular weights were determined by the Regnault method. Mass spectra were obtained by an Italelectronica SP 21F spectrometer at normal working conditions.⁷ Nuclear magnetic resonance spectra were made with a Varian 40 Mc. spectrometer model 4310C; determinations were made directly on the oscilloscope by the side-band method, with trifluoroacetic acid as standard.

Procedure.—Large-scale preparations were carried out in 2—3-l. Pyrex flasks by γ -irradiation of freshly prepared 1 : 1 mixtures of tetrafluoroethylene and oxygen at a total pressure of about 760 mm. The gaseous fraction was separated from the non-volatile liquid and distilled in a Podbielniak column. The products were further purified by gas chromatography. The retention times referred to tetrafluoroethylene in the column of Celite and perfluorotributylamine is 1.41 for tetrafluoroethylene oxide and 4.16 for perfluorocyclopropane.

X-Ray irradiations were performed in cells wholly of aluminium. Pyrex ampoules with break-seals were used for the γ -irradiations and for thermal reactions. The photochemical experiments were made in quartz ampoules (~100 c.c.). The reaction mixtures was analysed by infrared spectrophotometry. The absorption bands used for the quantitative determination of the products were 970 cm.⁻¹ for carbonyl fluoride, 1610 cm.⁻¹ for tetrafluoroethylene oxide, 870 cm.⁻¹ for hexafluorocyclopropane, and 1330 cm.⁻¹ for tetrafluoroethylene. All analyses \pm ca. 5%.

Carbonyl Fluoride.—This was characterized by its infrared spectrum.⁸

² R. L. Myers, *Ind. Eng. Chem.*, 1953, **45**, 1783.

³ R. N. Haszeldine and F. Nyman, *J.*, 1959, 1084.

⁴ D. Ambros, *Chem. průmysl*, 1960, **11**, 60 (*Chem. Abs.*, 1961, **55**, 18,556).

⁵ F. R. Mayo, *J. Amer. Chem. Soc.*, 1958, **80**, 2465.

⁶ D. Cordischi, A. D. Site, M. Lenzi, and A. Mele, *Chimica e Industria*, 1962, **44**, 1101.

⁷ A. Giardini-Guidoni and G. G. Volpi, *Nuovo cim.*, 1960, **17**, 919.

⁸ J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, 1954, Vol. II.

TABLE 3.

Relative ion intensity for a 80-v accelerating electron potential at the ion source of 10^{-6} torr.

Ion	<i>m/e</i>	(CF ₂) ₃	(CF ₂) ₂ O	Ion	<i>m/e</i>	(CF ₂) ₃	(CF ₂) ₂ O	Ion	<i>m/e</i>	(CF ₂) ₃	(CF ₂) ₂ O
CO ⁺	28		1.50	C ₂ F ₃ ⁺	62	1.04		C ₃ F ₃ ⁺	93	1.74	
CF ⁺	31	37.90	18.00	CF ₂ O ⁺	66		2.54	C ₂ F ₄ ⁺	100	88.30	7.12
CFO ⁺	47		65.50	CF ₃ ⁺	69	100	40.70	C ₃ F ₅ ⁺	131	16.50	
CF ₂ ⁺	50	14.40	100	C ₂ F ₅ ⁺	81	9.88		C ₃ F ₆ ⁺	150	1.39	

Tetrafluoroethylene Oxide.—This was isolated by distillation and purified by gas chromatography (b. p. -62°). We found that the product (M 115 ± 2) has a tendency to isomerize to give trifluoroacetyl fluoride, but the precise conditions have not yet been established.⁹

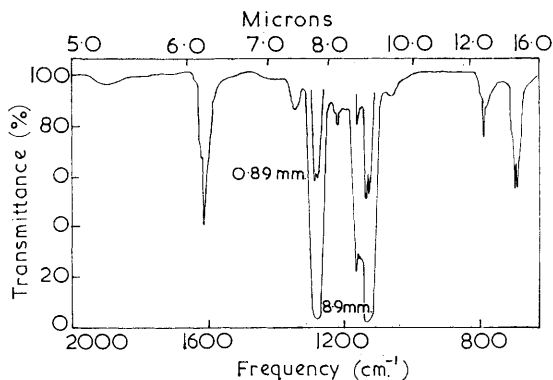
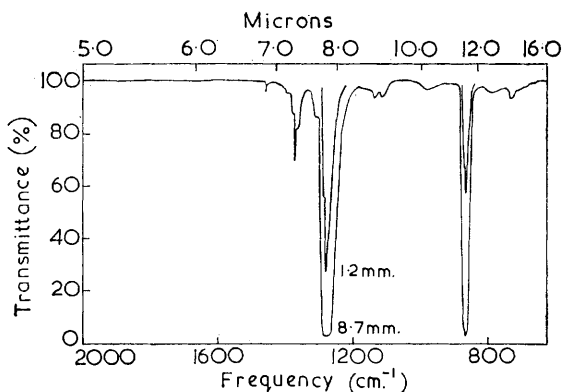


FIG. 1. Infrared spectra of tetrafluoroethylene oxide (gas).

FIG. 2. Infrared spectrum of hexafluorocyclopropane (gas).



The infrared spectrum (Fig. 1) does not correspond to that of trifluoroacetyl fluoride and the characteristic band of the carbonyl group at about 5.5μ is absent. The strong absorption band at 6.2μ is characteristic of the epoxide group, as found also for other fluorinated epoxides.^{3,10} The mass spectrum (Table 3) indicates the presence of oxygen, and the masses found do not contain more than two carbon atoms. The nuclear magnetic resonance (n.m.r.) spectrum gives a single band at about $+3.4 \delta$: this chemical shift is the same as that found for a CF₂ group bound to oxygen.¹¹

Hexafluorocyclopropane.—The compound obtained by chromatographic separation gave the correct molecular weight. The infrared spectrum (Fig. 2) differs from that of hexafluoropropene, is very similar to the spectra of other cyclic fluorocarbons,⁸ and corresponds to that

⁹ M. Lenzi and A. Mele, unpublished work.

¹⁰ du Pont de Nemours, B.P. 904877/1962.

¹¹ F. C. Nachod and W. D. Phillips, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, 1962, Vol. II, p. 406.

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recorded¹² for hexafluorocyclopropane. The mass spectrum (Table 3) seems to confirm the hypothesis of a three-term fluorocarbon. The n.m.r. spectrum shows a single line at $+75 \delta$ and this corresponds to the CF_2 resonance in a three-membered ring structure.¹¹

Liquid Polymeric Peroxide.—The liquid product separated from the volatile gaseous fraction has vapour pressure <1 mm. (Found: C, 18.7, 18.3; F, 54.0, 57.5; O, 26.9, 24.2. $\text{C}_2\text{F}_4\text{O}_2$ requires C, 18.2; F, 57.6; O, 24.2%). It was obtained by γ -irradiation of the mixture at room temperature after complete consumption of tetrafluoroethylene. The peroxidic character was revealed by reaction with a solution of sodium iodide in acetic anhydride.³ The n.m.r. spectrum shows a major band at about -23.35δ accounting for more than 90% of the total area and indicates the presence of only CF_2 groups bound to oxygen atoms. The spectrum does not show high bands at positive values of δ as normally found in totally fluorinated hydrocarbons. The minor bands may be due either to imperfections of the polymeric peroxide or to terminal groups. The infrared spectrum shows a large band between 1030 and 1350 cm^{-1} , and a small one in the carbonyl region at 1900 cm^{-1} , which can presumably be attributed to partial hydrolysis.

A small amount ($<1\%$) of an unidentified product was separated by gas chromatography from the high-boiling fraction. Its molecular weight was about 165—175 and the mass spectrum showed the presence of oxygenated fragments. The infrared spectrum shows two main bands at 1200 and 1260 cm^{-1} and no bands where carbonyl groups are usually found.

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¹² R. N. Haszeldine, *J.*, 1953, 3761.
