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OXIDATION REACTIONS OF TETRAFLUOROETHYLENE AND THEIR PRODUCTS—I

AUTO-OXIDATION*

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Abstract—Tetrafluoroethylene reacts with molecular oxygen in the dark and at low temperature to give an explosive rubber-like polymer, which has the structure $(CF_2-CF_2-O-O)_n$, together with minor amounts of tetrafluoroethylene oxide, carbonyl fluoride and perfluorocyclopropane. The reaction is strongly accelerated by ozone. Some reactions of tetrafluoroethylene oxide are also described.

The oxidation of olefins by molecular oxygen has been investigated with interest since the last century. Several reaction mechanisms have been proposed, but the complexity of the products, depending on experimental conditions, the nature of the starting material and the extent of the reaction, has made rationalization of the subject difficult.[1]

In the last decade Mayo and Miller[2-4] have made remarkable progress in their studies on the oxidation of olefins containing reactive double bonds as distinct from those having an active allylic hydrogen. In spite of the greater simplicity of reactions involving perhalo-olefins, little has been done in this field,[2] the only interest in the tetrafluoroethylene–oxygen system being its tendency to explode.[5,6]

Two polymers were occasionally obtained during work with tetrafluoroethylene in this laboratory and were both found to contain carbon, fluorine and oxygen only. While one of them is violently explosive, the other is exceptionally stable to heat. The latter has a molecular formula $(C_2F_4O)_n$.

While this work was in progress, a few patents[7,8] and papers[9,10] on the oxidation of tetrafluoroethylene were published.

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* This work has been presented at the *3rd International Symposium on Fluorine Chemistry*. Munich, 30th August–2nd September (1965).

[1] D. Swern, *Autooxidation and antioxidants* (Edited by W. O. Lundberg) Vol. I; Chap. 1, Interscience, New York (1961).

[2] F. R. Mayo, *J. Amer. Chem. Soc.* **80**, 2497 (1958) and Refs. cited therein.

[3] F. R. Mayo, A. A. Miller and G. A. Russell, *J. Amer. Chem. Soc.* **80**, 2,500 (1958).

[4] E. G. E. Hawkins, *Organic peroxides* p. 388, E. and F. F. Spon (1961).

[5] Ryo Kiyama, Jiro Osugi and Sigeru Kusuhara, *Rev. Phys. Chem. Japan* **27**, 22 (1957).

[6] Hiroshi Teranishi, *Rev. Phys. Chem. Japan* **28**, 9 (1958).

[7a] H. H. Gibbs and J. L. Warnell, Fr. Pat. 1.322.597 (Feb. 18, 1963 to E. I. DuPont de Nem.); [b] J. L. Warnell, US Pat. 3.125.599 (Mar. 17, 1964 to E. I. DuPont de Nem.); [c] J. L. Warnell, Fr. Pat. 1.342.523 (Sept. 30, 1963 to E. I. DuPont de Nem.).

[8] F. Gozzo and G. Carraro, Bel. Pat. 657.823 (Dec. 31, 1964 to Soc. Edison).

[9a] 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).

[10] F. Gozzo and G. Carraro, *Nature, Lond.* **206**, 507 (1965).

In Part II the photochemical oxidation of tetrafluoroethylene will be described.[11]

RESULTS

The auto-oxidation of tetrafluoroethylene was carried out in Pyrex sealed tubes, with a tetrafluoroethylene-oxygen molar ratio varying between 0·2 and 2. The temperature was kept between −80° and +20° and the amounts of the reactants were calculated so that the pressure never exceeded 15 atm. Both reagents being gaseous, the reaction was very slow and after a week a trace of a liquid polymer was formed, but no volatile organic products could be detected. In the presence of liquid tetrafluoroethylene a slow reaction took place with formation of a rubber-like polymer. Apparently long induction periods were necessary and the rate of the reaction was not reproducible. However, in most of the runs polymerization appeared complete after a couple of weeks at −10° and a pressure of ca. 13 atm (see run 1 of Table 1). If the oxygen contained small amounts of ozone, the reaction was much faster and practically complete after a period varying from a few days to a few minutes, depending on the concentration of ozone. When this latter was greater than approximately 0·5 moles % of O_2 it was necessary to keep the sealed tubes at low temperatures to avoid dangerous overheating of their contents.

Analysis of the products showed that tetrafluoroethylene and oxygen react in an approximately 1:1 molar ratio to give mainly an explosive copolymer, together with volatile products, such as, tetrafluoroethylene oxide, carbonyl fluoride, and small amounts of perfluorocyclopropane. It was also clear that ozone only acts as an effective initiator of the reaction.

As explosions were possible during isolation of the polymer it was found convenient to carry out the reaction in the presence of perfluorinated solvents, namely hexafluorobenzene and perfluoromethylcyclohexane. The polymer thus obtained was partly dissolved and partly swollen in these solvents, and could be handled without any special care.

The same polymer was obtained by bubbling a stream of oxygen, containing ca. 4 moles of O_3%, through tetrafluoroethylene solutions in "Freons" at −80°. After about 40 min a fluffy precipitate was noticed when a flow rate of 7·8 l./hr of O_2 was used.

As all attempts to analyse the copolymer resulted in a violent explosion, use was made of the conventional reduction of peroxidic bonds by a glacial acetic acid solution of 57 % hydroiodic acid, which was added with stirring to hexafluorobenzene solutions of the polymer at room temperature. The reaction was complete in a few hr to give iodine, oxalic acid, carbon dioxide and hydrogen fluoride. Many identical runs were carried out but the results were erratic, even when the reduction was performed separately and under similar conditions on the same sample divided into two parts. Iodine and oxalic acid were always formed in approx. a 1:1 molar ratio and in amounts varying between 0·5 and 1·1 equivs per 100 g of the polymer. Thus between 30 and 75% by wt of it reacted as a sequence of (CF_2—CF_2—O—O) units, the remainder being decomposed directly to COF_2.

In spite of these irreproducible results both the IR[10] and the NMR spectra of samples of the polymer were always the same, even when the analytical reduction gave widely different results. In particular, the NMR spectrum of the polymer

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[11] F. Gozzo and G. Camaggi, *Tetrahedron*, to be published.

TABLE 1. EXPERIMENTS OF AUTO-OXIDATION

					Reactants				Products*			
	Sealed tube		Tubes opened		(mmoles)		Solvent		(mmoles)			(g)
Run No.	volume (ml)	Temp	after (days)	O_2	O_3	C_2F_4	(C_6F_6) (g)	O_2	C_2F_4	C_2F_4O	COF_2	$-(CF_2-CF_2-O-O)-_n$
1	17	−10°	7	10·2	—	20·5	—	0·1	8·4	n.c.	n.c.	exploded
2	33	+15°	5	24·5	0·03	24·5	8·3	1·3	tr	5·8	4·1	1·4–1·6
3	33	−80°	4	24·2	0·03	23·6	7·9	4·4	2·7	6·1	5·4	1·6
4	33	+15°	8	18·1	0·3	4·2	2·7	14	—	tr	0·6	0·5
5	33	−15°	2	38·8	0·05	24·4	11	32·9	14·4	0·4	0·8	1
6	33	−20°	2	45·1	0·06	24·4	8·3	34·8	9·9	1·4	1·6	1·4–1·5
7	33	−15°	3	45·1	0·06	24·4	8·1	25·5	1·6	3·9	3·3	2·1–2·3

* Perfluorocyclopropane was always present in traces.

dissolved in hexafluorobenzene, displayed a main signal at +14·6 ppm with respect to CF_3—COOH.* Since this signal accounted for more than 80–90% of the resonating nuclei it was clear that the polymer was structurally homogeneous.

The combined evidence resulting from both the physical and the chemical methods indicated that the polymer has mainly the poly(tetrafluoroethylene peroxide) structure.

While this work was in progress, some chemical and mechanical properties of the copolymer were described by Pajaczkowski and Spoors.[12]

Tetrafluoroethylene oxide, separated by distillation from other volatile products of the reaction, reacts slowly with water to give oxalic acid and hydrogen fluoride quantitatively, and was found to be very sensitive to nucleophilic attack. Thus with potassium fluoride it isomerized to trifluoroacetyl fluoride. Reactions with ethyllithium and ethylmagnesium bromide gave very complex mixtures of products, from which no definite compound could be isolated. On treatment with diethylamine a compound, probably 2-diethylamino-2,2-difluoro-N,N-diethylacetamide, was obtained which was easily hydrolysed to N,N,N',N'-tetraethyloxamide.

All attempts to polymerize tetrafluoroethylene oxide by conventional methods failed. Small amounts of oligomers were obtained by passing a high-frequency electrical discharge through the frozen epoxide. The IR spectrum of this product was similar to that of the polymer with molecular formula $(C_2F_4O)_n$ described in the introduction. The NMR spectrum of the latter dissolved in hexafluorobenzene displayed a strong signal at +12·3 ppm with respect to trifluoroacetic acid.†

The only suitable method to obtain a high-molecular-weight polymer from the epoxide is by gamma-ray irradiation of the solid monomer kept in liquid nitrogen, as described in a recent patent by DuPont.[7c]

DISCUSSION

The reaction of tetrafluoroethylene with molecular oxygen in the dark and at low temperature shows features typical of the classical auto-oxidation of olefins with a reactive double bond.[2,13] The acceleration of the reaction by traces of ozone is in line with the general radical initiation of the copolymerization of olefins with oxygen. When no initiators are added to the system, nothing can be said about the initiation phase because of the non-reproducibility of the reaction rate. The lack of evidence for the presence of volatile peroxides may preclude a direct interaction between molecular oxygen and tetrafluoroethylene. On the other hand, even the most thorough investigations on the direct reaction between olefins and molecular oxygen, have left the problem of the initiation phase unsolved.[14]

Under the experimental conditions used those which promote the chain reaction

$$\sim CF_2\cdot + O_2 \rightarrow \sim CF_2—O—O\cdot \tag{1}$$

$$\sim CF_2—O—O\cdot + C_2F_4 \rightarrow \sim CF_2—O—O—CF_2—CF_2\cdot \tag{2}$$

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* Calculated by using hexafluorobenzene as internal standard ($\Delta^{C_6F_6}_{CF_3COOH} = 88{\cdot}4$ ppm.).

† Calculated by using hexafluorobenzene as internal standard.

[12] A. Pajaczkowski and J. W. Spoors, *Chem. & Ind.* **16,** 659 (1964).

[13] See Ref. 4, Chaps 8 and 12.

[14] N. Uri, *Autooxidation and antioxidants* (Edited by W. O. Lundberg) Chap. 2, Interscience (1961).

predominate over those inducing cleavage reactions which afford tetrafluoroethylene oxide and carbonyl fluoride.

$$-\!(CF_2-CF_2-O-O)\!-_n CF_2-CF_2\cdot \rightarrow -\!(CF_2-CF_2-O-O)\!-_{n-1} CF_2-CF_2-O\cdot + C_2F_4O \quad (3)$$

$$-\!(CF_2-CF_2-O-O)\!-_n CF_2-CF_2-O\cdot \rightarrow -\!(CF_2-CF_2-O-O)\!-_n CF_2\cdot + COF_2 \quad (4)$$

This may be due to the limited number of wall collisions together with the high concentration of the reagents in the condensed phase. The cleavage reaction of the copolymer to give carbonyl fluoride takes place easily during its reduction with aqueous hydrogen iodide, which gives erratic results. This is not surprising since iodometric reduction of other organic polyperoxides are known to be unsatisfactory.[15,16]

Therefore the characterization of poly(tetrafluoroethylene peroxide) was based on the molar ratio (ca. 1:1) according to which tetrafluoroethylene and oxygen react to give the copolymer, together with the identity of the NMR spectra of different samples, the reduction of which gave widely different results.

EXPERIMENTAL

Auto-oxidation

Tetrafluoroethylene was prepared by pyrolysis of chlorodifluoromethane and purified by fractional distillation. Commercial-grade O_2, dried over P_2O_5 was used and, in most of the runs, ozonized by passing it through a Labor-Ozonisator O_{z2} (Demag Elektrometallurgie).

Tetrafluoroethylene and O_2 were condensed in Pyrex tubes (mostly in the presence of few grams hexafluorobenzene) provided with a long capillary neck. This could be easily sealed and opened at the end of the reaction inside a piece of rubber tubing connected to a large glass container of known volume kept under vacuum, where the volatile products were collected. Hexafluorobenzene solutions of poly(tetrafluoroethylene peroxide) were highly viscous and could be taken out of the tubes only after further dilution. The IR spectrum of a film of the polymer displayed 3 main broad bands between 7·75 and 9·75 μ.

The reduction of hexafluorobenzene solutions of poly(tetrafluoroethylene peroxide) was carried out by adding a slight excess of 57% HIaq (1 part) and glacial AcOH (10 parts) usually at room temp. The whole apparatus was swept with He and the CO_2 evolved during the reaction was absorbed by standard $Ba(OH)_2$.

The volatile products of the reaction were analysed and separated by GLC. The column, 12-m long and 4 mm in diameter, was packed with bis(2-ethylhexyl)sebacate supported on Kieselghur and kept at −9°. He was used as the carrier gas.

Usually the components of the mixture were O_2, tetrafluoroethylene, tetrafluoroethylene oxide, COF_2 and perfluorocyclopropane in order of increasing retention times. COF_2 was completely converted into CO_2 on passing through the column and was identified as such in the mixture by IR spectroscopy. All the other components were identified by comparing their IR spectra with those of authentic specimens.

Tetrafluoroethylene oxide

The combined volatile products from several runs (20 g) were freed from COF_2 and CO_2 by a preliminary fractional distillation using a column with a wide still-head. The residue (9 g) was fractionally distilled through a Podbielniak column to give tetrafluoroethylene oxide (5 g), the properties of which were identical with those reported in the literature.[7a,8a,9a]

(a) Tetrafluoroethylene oxide (11 mmoles) and KF (1 g) were placed into a 15 ml autoclave, and heated at 80° for 4 hr. The product was collected in a trap cooled by liquid N_2 and found to be mostly trifluoroacetyl fluoride (IR).

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[15] F. A. Bovey and I. M. Kolthoff, *J. Amer. Chem. Soc.* **69**, 2143 (1947).

[16] A. A. Miller and F. R. Mayo, *J. Amer. Chem. Soc.* **78**, 1017 (1956).

(b) Tetrafluoroethylene oxide (10 mmoles) was shaken with water (100 g) at 20° for 24 hr to give oxalic acid, as determined by titration with 0·1N $KMnO_4$ (200 ml) and HF (0·8 g) quantitatively.

(c) Tetrafluoroethylene oxide (10 g) was added to a mixture of anhydrous ether (200 ml) and diethylamine (30 g) kept at −80° under vigorous stirring. After 2 hr the temp was allowed to rise slowly up to 20° and the reaction mixture filtered to remove diethylammonium fluoride. Ether was mostly removed by distillation and the residue distilled *in vacuo* (74°/2 mm Hg) to give a viscous, colourless liquid (12·53 g), which turned brown on keeping. Its elemental analysis was not quite correct for 2-diethylamino-2,2-difluoro-N,N-diethylacetamide. (Found: C, 54·6; H, 9·3. $C_{10}H_{20}F_2N_2O$ requires: C, 54·0; H, 9·0%.) However its IR spectrum was consistent with the anticipated structure and displayed a carbonyl stretching band at 5·95 μ. A sample of this compound (5 g) was treated with 50% KOHaq (20 ml) and heated to 80°. A violent reaction took place, the organic phase decolorized and was subsequently separated and distilled *in vacuo* (98°/2 mm Hg) to give N,N,N′,N′-tetraethyloxamide (4 g), identified by comparing its IR spectrum with that of an authentic specimen.

(d) Tetrafluoroethylene oxide (15 g) was added under vigorous stirring to a solution of EtLi (33·4 g) in anhydrous ether (350 ml) at −60°. A vigorous reaction took place and after 1 hr the temp was allowed to rise slowly up to 20°. A concentrated ammonium chloride solution (300 ml) was added very slowly to the reaction mixture under stirring. The ethereal layer was separated, the aqueous one was continuously extracted with ether and the combined layer and extracts were dried ($MgSO_4$) and ether removed by distillation. The residue was distilled *in vacuo* (boiling range 40°–110/20 mm Hg) and shown to be a mixture of at least ten components by GLC. Its IR spectrum showed broad bands in the alcoholic hydroxyl and ketonic carbonyl stretching regions. All attempts to isolate some pure component failed.

Under identical conditions tetrafluoroethylene oxide was made to react with EtMgBr. The crude product had the same IR spectrum as that from the EtLi reaction.

(e) Attempts were made to polymerize tetrafluoroethylene oxide by using several reagents.

1. With BF_3, no reaction took place at low temp and at 50° and 30 atm rearrangement to trifluoroacetyl fluoride was observed.
2. With 1% C_4H_9Li in *n*-pentane in a sealed tube at −80°, the epoxide was recovered unchanged.
3. With $CaCO_3$ (0·116 g) and perfluoromethylcyclohexane (2·49 g) and epoxide (2·3 g) at −40° in a shaken sealed tube there was no reaction.
4. With NF_3 or $(CF_3)_2NF$ and UV light at room temp and at −60°, partial conversion to COF_2 and minor volatile products was observed.
5. With $B(C_2H_5)_3$ and traces of O_2 in a sealed tube at −60° up to room temp, the epoxide was recovered unchanged.
6. With a high frequency discharge from a Tesla on the solid epoxide kept at −190°, most of the epoxide was recovered unchanged after a few hr. Only a few drops of an acrid-smelling substance, the IR spectrum of which was nearly identical with that of an authentic specimen of poly(tetrafluoroethylene oxide).[7c] was obtained.

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