Kinetics and Mechanism of the Thermal Gas-Phase Oxidation of Perfluorobutene-2 in Presence of Trifluoromethyl Hypofluorite

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ABSTRACT: The oxidation of perfluorobutene-2 (C_4F_8) initiated by trifluoromethyl hypofluorite (CF_3OF) in presence of O_2 has been studied at 323.1, 332.6, 342.5, and 352.0 K, using a conventional static system. The initial pressure of CF_3OF was varied between 4.8 and 23.6 Torr, that of C_4F_8 between 48.7 and 302.4 Torr, and that of O_2 between 51.5 and 270.4 Torr. Several runs were made in presence of 325.5–451.2 Torr of N_2. The main products were COF_2, $CF_3C(O)F$, and $CF_3OC(O)F$. Small amounts of compound containing —$CF(CF_3)$—O—$C(O)CF_3$ group were also formed, as detected by ^{13}C NMR spectroscopy. The oxidation is a homogeneous short-chain reaction, attaining, at the pressure of O_2 used, the pseudo-zero-order condition with respect to O_2 as reactant. The reaction is independent of the total pressure. Its basic steps are as follows: the thermal generation of $CF_3O^{\bullet}$ radicals by the abstraction of fluorine atom of CF_3OF by

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C_4F_8, the addition of $CF_3O^{\bullet}$ to the alkene, the formation of perfluoroalkoxy radicals $RO^{\bullet}$ in presence of O_2, and the decomposition of these radicals via the C—C bond scission, giving products containing —C(O)F end group and reforming $RO^{\bullet}$ and $CF_3O^{\bullet}$ radicals. The mechanism consistent with experimental results is postulated. © 2003 Wiley Periodicals, Inc. Int J Chem Kinet 35: 532–541, 2003

INTRODUCTION

In recent years the fluorine chemistry has been continuously growing in areas such as new fluoropharmaceuticals, nonsoluble, noncorrosive biocompatible materials for implants in medicine, agrochemicals, alternative refrigerants, paints, electronics, surface coatings for corrosion and moisture protection, and high performance lubricants.

The fluid perfluoropolyethers are used as lubricants for the computer hard disks because of their good performance as a protective layer between the hard disk surface and the magnetic head. The major route utilized for their commercial production is the photooxidation [1–5] of perfluoroolefins (CF_2CF_2, CF_3CFCF_2) in liquid phase at 233 K or lower, initiated by UV light. These lubricants are mixtures of species with different relative molecular masses, containing —CF_2—O— and —$CF(CF_3)$—O— groups.

In the gas-phase photooxidation of perfluoropropene at 303 K [2], the main reaction products reported were COF_2, $CF_3C(O)F$, $CF_3OC(O)F$, and $CF_3OCF_2C(O)F$ and a mixture of two series of telomers, $CF_3O(CF_2O)_nC(O)F$ and $CF_3O(CF_2O)_nCF_2C(O)F$, where $n = 1$–12. The formation of $CF_3C(O)F$ and $CF_3OC(O)F$ was observed in the mercury-photosensitized oxidation of perfluorobutene, C_4F_8 [6].

It was found that in the photooxidation of liquid hexafluorobutadiene, C_4F_6, more than 50% of diolefin was converted, through a kinetically complicated process, into a high relative molecular mass liquid polyethers, having a complex chain structure with C(O)F end group [2,7].

The use of chemical initiators, instead of UV light, for synthesis of perfluoropolyethers has significant practical and technological advantages. It is an interesting alternative offering a better control over the structure and relative molecular mass of the products. The possibility of synthesis of simpler molecules provides useful tools for the studies of the unique properties of perfluoropolyethers attributed to their different segments and end groups. The chemical initiator must be able to generate free radicals that should be either capable of direct addition to the double bond or to do so after their reaction with oxygen. Recently the fluorine-initiated liquid-phase oxidation of C_2F_4 was reported in the literature [7,8].

The stable and easily handled trifluoromethyl hypofluorite, CF_3OF, containing a weak O—F bond, is a versatile and selective fluorinating agent [9]. The value of 43.5 kcal mol^{-1} was determined for the dissociation energy of O—F bond [10–12]. The thermal addition of CF_3OF across the double bond of a variety of olefins belongs to a very interesting class of reactions, where a saturated compound with a relatively weak bond initiates a series of reactions, important from the synthetic and mechanistic point of view.

In this work the investigation of the thermal gas-phase oxidation of C_4F_8 in the presence of CF_3OF has been undertaken to study the use of chemical initiators in the oxidative processes of fluoroolefins, leading to the formation of compounds containing the C—O—C ether groups.

EXPERIMENTAL

The reaction proceeded with pressure decrease. The experiments were performed in a grease-free static system allowing pressure measurements at constant volume and temperature. Two reaction vessels were used: a spherical quartz bulb with a volume of 270 cm^3 (surface-to-volume ratio, S/V = 0.75 cm^{-1}) and another one of similar dimension filled with small pieces of quartz tubing (S/V = 4.7 cm^{-1}). The pressure was measured with a quartz spiral gauge and the temperature maintained within ±0.1 K using a Lauda thermostat. Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer and a Perkin-Elmer 1600 Series FTIR spectrometer, using 10-cm cells provided with NaCl and KBr windows, respectively. The resolution of the reported wave numbers was 1 cm^{-1}.

All reactants were purchased commercially. CF_3OF (PCR, 97–98%) was washed with 0.1 mol dm^{-3} NaOH solution and filtered at 80 K [13]. C_4F_8 (PCR, 97–98%) was purified by repeated low-pressure trap-to-trap distillations on a vacuum line, the middle fraction being retained each time. The purified reactants were spectroscopically pure. O_2 (La Oxigena, 99.99%) and N_2 (La Oxigena, 99.9%) were bubbled through 98% analytical-grade H_2SO_4, and passed slowly through a Pyrex coil at 153 K and at liquid-air temperature, respectively.

The reaction was followed, measuring the consumption of C_4F_8 as a function of time. Twenty-nine

experiments were carried out at 323.1, 332.6, 342.5, and 352.0 K. The initial pressure of CF_3OF was varied between 4.8 and 23.6 Torr, that of C_4F_8 between 48.7 and 302.4 Torr, and that of O_2 between 51.5 and 270.4 Torr. Several experiments were carried out in presence of 325.5–451.2 Torr of N_2. Two experiments were carried out in the reactor with $S/V = 4.7\ cm^{-1}$.

The reaction is a homogeneous chain reaction, with a very short chain length. Its course does not change on increasing the surface-to-volume ratio. Under the conditions of our work the reaction was independent of the total pressure and attained the pseudo-zero-order condition with respect to O_2 as reactant.

In absence of CF_3OF, no reaction was observed between C_4F_8 and O_2 after several hours.

In presence of CF_3OF, the following products were detected by infrared spectroscopy: COF_2 [14], $CF_3C(O)F$ [15], and $CF_3OC(O)F$ [16–18]. Small amounts of an unknown compound X, containing $-CF(CF_3)OC(O)CF_3$ group, were also formed, as detected by ^{13}C NMR spectroscopy.

In the ^{13}C NMR spectrum of a sample containing the unknown compound X ($C(1)F_3C(2)(O)OC(3)FC(4)F_3-$), obtained at room temperature and in a $CDCl_3$ solution, using a Bruker AC 250 NMR spectrometer, four signals were observed: $\delta = 114.49$ ppm (c, C(1), $^1J_{CF} = 284.67$ Hz), $\delta = 161.79$ ppm (c, C(2), $^2J_{CF} = 43.87$ Hz), $\delta = 137.04$ ppm (cd, C(3), $^1J_{CF} = 296.59$ Hz, $^2J_{CF} = 2.86$ Hz), $\delta = 119.04$ ppm (dc, C(4), $^1J_{CF} = 269.65$ Hz, $^2J_{CF} = 10.96$ Hz).

No absorption bands between 1450 and 1650 cm^{-1} were found in the infrared spectra obtained. It indicates that the perflurobutene epoxide, $CF_3CF\overset{O}{\frown}CFCF_3$, did not form in the reaction course. A strong absorption band in this frequency range is characteristic of perfluorinated olefin epoxides, not being produced by other perfluorocarbon compounds. Neither was the very strong band of CF_3OOCF_3 at 1166 cm^{-1} [19,20] observed.

To analyze the reaction mixture of each experiment and to follow the consumption of the reactants as a function of time, the reaction vessel was rapidly cooled to liquid-air temperature at selected intervals of reaction time and the mixture separated by fractional condensation. The nonconsumed O_2 and any N_2, if present, were separated as volatile at liquid-air temperature as the first fraction Fr_1. The second fraction Fr_2, volatile at 123 K, consisted of CF_3OF and COF_2. To determine the concentration of COF_2 in this fraction, an infrared calibration curve was obtained using the pure compound, thereby allowing conversion of the absorption intensity at 1942 cm^{-1} to the pressure of COF_2. The amount of CF_3OF was obtained by difference. In the third fraction Fr_3, volatile at 163 K, in addition to the infrared absorption bands of $CF_3OC(O)F$, a small band at 1830 cm^{-1} was also observed. It can be attributed to the C=O group present in the $-CF(CF_3)OC(O)CF_3$ group of the product X. It was reported that the absorption band corresponding to C=O group of the compound $(CF_3)_2C(F)OOC(O)CF_3$ appeared at 1849 cm^{-1} [21]. The fourth fraction Fr_4, remaining as residue at 163 K, consisted of nonconsumed perfluorobutene.

The amounts of CF_3OF consumed correspond closely to the calculated ones using the expression $[CF_3OF]_{consum} = [CF_3OF]_i \times \{1 - \exp(-k_1 \Delta t [C_4F_8]_m)\}$, where Δt is the reaction time, $[C_4F_8]_m$ is the mean pressure of perfluorobutene within the interval Δt, and $k_1 = (5.34 \pm 0.3) \times 10^6 \exp(-(13.9 \pm 0.8)\ kcal\ mol^{-1}/RT)\ dm^3\ mol^{-1}\ s^{-1}$ is the rate constant for the gas-phase addition of CF_3OF to the double bond of C_4F_8 in absence of O_2, obtained previously [22].

RESULTS

The analytical data of 23 selected experiments are summarized in Table I.

The reaction mechanism proposed to explain the experimental results is presented in Table II. In this mechanism the considered telomerization steps, initiated by the addition of radical $CF_3OC(O)^{\bullet}FCF_3$ to olefin and giving $CF_3O(CF(CF_3)O)_nC(O)F$, where $n = 1,2\ldots$, were not included. These telomerization steps should occur only to a very small extent, not affecting substantially the interpretation of the experimental results.

The corresponding global reaction for telomerization can be written as

$$CF_3OC(O)^{\bullet}FCF_3 + nCF_3CFCFCF_3 + nO_2 \rightarrow CF_3O(CF(CF_3)O)_nC(O)F + nCF_3C(O)F + CF_3^{\bullet}$$

It was reported that the fluoroformate group of the perfluoropolyethers containing $C(CF_3)F-O-C(O)F$ end group decomposes thermally to give $-C(O)CF_3$ group and $C(O)F_2$ [2]; then the formation of compound X containing $-C(CF_3)F-O-C(O)-CF_3$ group can be explained by the following global reaction:

$$CF_3O(CF(CF_3)O)_nC(O)F \rightarrow CF_3O(CF(CF_3)O)_{n-1}C(O)CF_3 + COF_2$$

where $n = 2$.

Applying the steady-state approximation to the proposed mechanism, the following expressions were obtained for the consumption of perfluorobutene-2 (C_4F_8)

Table I Analytical Data of 23 Experiments

No. of Run	T (K)	Δt (min)	CF_3OF_i (Torr)	CF_3OF_f (Torr)	C_4F_{8i} (Torr)	C_4F_{8f} (Torr)	O_{2i} (Torr)	O_{2f} (Torr)	P_1 (Torr)	P_{2+3} (Torr)	P_4 (Torr)
26	323.1	303.9	19.8	16.4	97.8	88.8	81.3	70.0	13.0	4.6	3.3
27	323.1	237.0	12.0	10.4	89.3	85.5	81.1	76.6	6.1	1.4	1.5
28	323.1	449.8	11.5	10.5	58.8	54.1	51.5	45.9	7.2	1.8	1.4
2	332.6	27.0	23.6	22.4	94.8	92.8	270.4	268.4	3.8	0.4	0.8
3	332.6	358.6	14.6	6.4	204.8	183.6	154.8	130.6	35.8	6.0	8.0
4	332.6	226.2	13.0	9.0	100.3	92.7	99.1	91.1	14.0	0.8	3.4
22	332.6	123.3	19.5	16.5	100.5	93.6	102.0	93.9	11.0	2.4	2.5
23	332.6	124.0	13.4	8.8	302.4	289.5	153.6	138.2	20.0	5.0	4.5
24	332.6	191.0	8.5	5.3	198.9	191.3	150.6	142.1	13.0	1.8	3.0
6	342.5	188.0	14.2	8.6	100.6	84.6	118.0	99.2	26.0	5.6	5.3
7	342.5	181.3	11.7	5.5	202.5	184.3	149.8	128.3	29.0	6.6	6.0
8	342.5	298.5	6.5	2.0	200.6	186.2	150.6	133.8	23.4	4.8	4.5
9	342.5	187.0	20.0	16.8	48.7	37.9	77.5	63.9	15.4	5.6	3.1
10	342.5	130.0	19.7	15.1	102.2	88.0	106.9	89.4	21.2	6.6	4.4
11	342.5	239.4	4.8	3.1	88.0	83.3	100.6	95.5	8.4	0.8	1.7
12	352.0	134.8	11.0	7.0	102.4	86.4	111.6	91.4	22.8	8.4	3.9
13	352.0	70.5	19.1	14.9	100.9	84.7	113.6	93.2	23.2	8.4	3.9
14	352.0	170.8	11.3	8.7	51.2	38.9	69.2	53.1	16.2	7.6	2.4
15	352.0	195.4	6.5	3.4	102.1	89.0	101.7	85.1	18.4	7.0	3.1
16[a]	352.0	58.3	20.0	16.2	101.3	86.3	111.6	92.6	21.2	8.0	3.4
18	352.0	116.0	7.1	3.3	200.7	185.5	159.7	140.8	22.4	7.4	3.8
19	352.0	125.0	10.4	7.0	100.8	85.8	262.6	243.5	21.0	8.2	3.4
20[b]	352.0	59.8	19.9	16.0	101.5	86.3	109.0	89.7	21.4	8.2	3.5

Note: $P_1 = CF_3C(O)F$, $P_{2+3} = CF_3OC(O)F + X$, where X is the compound containing the ─CF(CF_3)─O─C(O)CF_3 group, and $P_4 = COF_2$. Δt is the reaction time. The subscripts i and f signify initial and final, respectively.

[a] 451.2 Torr of N_2 was present.

[b] The surface-to-volume ratio of the reaction vessel used in this experiment was 6.3 times greater.

Table II The Mechanism for the Oxidation of C_4F_2-2 Initiated by CF_3OF Proposed to Explain the Experimental Results

1. $CF_3OF + CF_3CF{=}CFCF_3 \rightarrow CF_3CF_2C^{\bullet}FCF_3 + CF_3O^{\bullet}$
2. $CF_3CF_2C^{\bullet}FCF_3 + O_2 + M \rightarrow CF_3CF_2C(O_2)^{\bullet}FCF_3 + M$
3. $CF_3CF_2C(O_2)^{\bullet}FCF_3 + RO_2 \rightarrow CF_3CF_2C(O)^{\bullet}FCF_3 + RO + O_2$
4. $CF_3CF_2C(O)^{\bullet}FCF_3 \rightarrow CF_3C^{\bullet}F_2 + \underline{CF_3C(O)F}$
5. $CF_3C^{\bullet}F_2 + O_2 + M \rightarrow CF_3CF_2O_2^{\bullet} + M$
6. $CF_3CF_2O_2^{\bullet} + RO_2 \rightarrow CF_3CF_2O^{\bullet} + RO + O_2$
7. $CF_3CF_2O^{\bullet} \rightarrow CF_3^{\bullet} + \underline{COF_2}$
8. $CF_3^{\bullet} + O_2 + M \rightarrow CF_3O_2^{\bullet} + M$
9. $CF_3O_2^{\bullet} + RO_2 \rightarrow CF_3O^{\bullet} + RO + O_2$
10. $CF_3O^{\bullet} + CF_3CF{=}CFCF_3 \rightarrow CF_3OCF(CF_3)C^{\bullet}FCF_3$
11. $CF_3OCF(CF_3)C^{\bullet}FCF_3 + O_2 + M \rightarrow CF_3OCF(CF_3)C(O_2)^{\bullet}FCF_3 + M$
12. $CF_3OCF(CF_3)C(O_2)^{\bullet}FCF_3 + RO_2 \rightarrow CF_3OCF(CF_3)C(O)^{\bullet}FCF_3 + RO + O_2$
13. $CF_3OCF(CF_3)C(O)^{\bullet}FCF_3 \rightarrow CF_3OC^{\bullet}FCF_3 + \underline{CF_3C(O)F}$
14. $CF_3OCF(CF_3)C(O)^{\bullet}FCF_3 \rightarrow CF_3^{\bullet} + CF_3OCF(CF_3)C(O)F$
15. $CF_3OC^{\bullet}FCF_3 + O_2 + M \rightarrow CF_3OC(O_2)^{\bullet}FCF_3 + M$
16. $CF_3OC(O_2)^{\bullet}FCF_3 + RO_2 \rightarrow CF_3OC(O)^{\bullet}FCF_3 + RO + O_2$
17. $CF_3OC(O)^{\bullet}FCF_3 \rightarrow CF_3^{\bullet} + \underline{CF_3OC(O)F}$
18. $CF_3CF_2O^{\bullet} + CF_3CF{=}CFCF_3 \rightarrow CF_3CF_2OCF(CF_3)C^{\bullet}FCF_3$
19. $CF_3CF_2OCF(CF_3)C^{\bullet}FCF_3 + O_2 + M \rightarrow CF_3CF_2OCF(CF_3)C(O_2)^{\bullet}FCF_3 + M$
20. $CF_3CF_2OCF(CF_3)C(O_2)^{\bullet}FCF_3 + RO_2 \rightarrow CF_3CF_2OCF(CF_3)C(O)^{\bullet}FCF_3 + RO + O_2$
21. $CF_3CF_2OCF(CF_3)C(O)^{\bullet}FCF_3 \rightarrow CF_3CF_2OC^{\bullet}FCF_3 + CF_3C(O)F$
22. $CF_3CF_2OC^{\bullet}FCF_3 + O_2 + M \rightarrow CF_3CF_2OC(O_2)^{\bullet}FCF_3 + M$
23. $CF_3CF_2OC(O_2)^{\bullet}FCF_3 + RO_2 \rightarrow CF_3CF_2OC(O)^{\bullet}FCF_3 + RO + O_2$
24. $CF_3CF_2OC(O)^{\bullet}FCF_3 \rightarrow CF_3^{\bullet} + \underline{CF_3CF_2OC(O)F}$
25. $R^{\bullet} + CF_3OF \rightarrow RF + CF_3O^{\bullet}$
26. $R^{\bullet} + R^{\bullet} \rightarrow$ Recombination products

In this mechanism $R^{\bullet} = CF_3^{\bullet}$, $CF_3C^{\bullet}F_2$, $CF_3CF_2C^{\bullet}FCF_3$, $CF_3OC^{\bullet}F(CF_3)$, $CF_3OCF(CF_3)C^{\bullet}FCF_3$, $CF_3CF_2OC^{\bullet}F(CF_3)$, or $CF_3CF_2OCF(CF_3)C^{\bullet}F(CF_3)$.

and that of CF_3OF:

$$-\mathrm{d}[C_4F_8]/\mathrm{d}t = -n\,\mathrm{d}[CF_3OF]/\mathrm{d}t = \lambda k_1[CF_3OF][C_4F_8] \quad \text{(I)}$$

$$-\mathrm{d}[CF_3OF]/\mathrm{d}t = k_1[CF_3OF][C_4F_8] + k_{25}[R^{\bullet}][CF_3OF] \quad \text{(II)}$$

where the kinetic chain length $\lambda = n\gamma$ is the ratio between the consumption rate of perfluorobutene and the rate of initiation $k_1[CF_3OF][C_4F_8]$, and γ is the ratio of the rate of consumption of CF_3OF to that of initiation.

Taking into account that the termination rate $k_{26}[R]^2$ is equal to that of initiation, and that reaction (7) is more rapid than reaction (18), the following expression was obtained for λ:

$$\lambda = (1 + k_{10}[CF_3O^{\bullet}])/k_1[CF_3OF] = n\{1 + k_{25}(k_1k_{26})^{-0.5}([CF_3OF]/[C_4F_8])^{0.5}\} \quad \text{(III)}$$

$$nk_1 = k = (\Delta[C_4F_8]/\Delta t)_{\mathrm{exp}}/\{[CF_3OF][C_4F_8] \times (1 + k_{25}(k_1k_{26})^{-0.5}([CF_3OF]/[C_4F_8])^{0.5})\} \quad \text{(IV)}$$

where $(\Delta[C_4F_8]/\Delta t)_{\mathrm{exp}}$ is the experimental consumption rate of C_4F_8.

The constants k at different temperatures were estimated plotting $(\Delta[C_4F_8]/\Delta t)_{\mathrm{exp}}/([CF_3OF][C_4F_8])$ as a function of $([CF_3OF]/[C_4F_8])^{0.5}$. Subsequently the constant k' equal to $k_{25}(k_1k_{26})^{-0.5}$ was determined as a slope, plotting $(m-1)$ vs. $([CF_3OF]/[C_4F_8])^{0.5}$, where $m = (\Delta[C_4F_8]/\Delta t)_{\mathrm{exp}}/k\,([CF_3OF][C_4F_8])$. The plot is illustrated in Fig. 1. As can be seen from this plot, k' is equal to 0.5 and does not depend on temperature.

In order to derive k_{25}, the rate constant for the abstraction of fluorine atom from CF_3OF by perfluoroalkyl radicals, from the value of k', k_{26} was assumed to be equal to the collisional frequency factor, 10^{10} dm^3 mol^{-1} s^{-1}, and k_1 was calculated using the expression obtained previously in the study of the thermal gas-phase addition of CF_3OF to C_4F_8 in absence of O_2 [22]:

$$k_1 = (5.34 \pm 0.3) \times 10^6 \exp(-(13.9 \pm 0.8)\ \text{kcal mol}^{-1}/RT)\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \quad \text{(V)}$$

The k_{25} values of $(2.32 \pm 0.7) \times 10^3$, $(3.16 \pm 0.9) \times 10^3$, $(4.27 \pm 1.2) \times 10^3$, and $(5.63 \pm 1.5) \times 10^3$

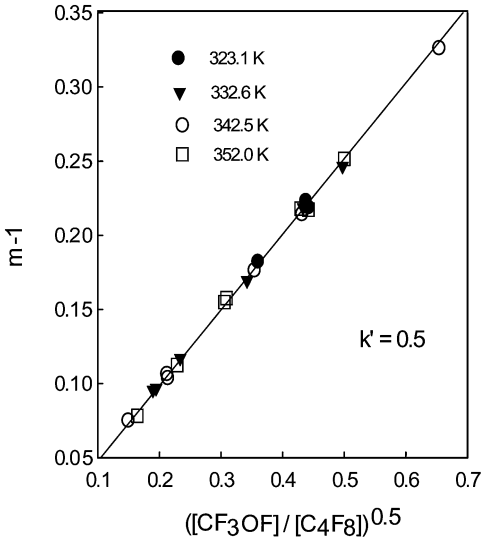

Figure 1 Plot of $(m-1)$ vs. $([CF_3OF]/[C_4F_8])^{0.5}$, where $m = (\Delta[C_4F_8]/\Delta t)_{exp}/k[CF_3OF][C_4F_8]$. The value of the slope is equal to $k' = k_{25}(k_1k_{26})^{-0.5}$.

$dm^3\ mol^{-1}\ s^{-1}$ were obtained at 323.1, 332.6, 342.5, and 352.0 K, respectively. The Arrhenius plot of k_{25} is illustrated in Fig. 2. The temperature dependence of k_{25} can be expressed by:

$$k_{25} = (1.14 \pm 0.5) \times 10^8 \exp(-(6.94 \pm 1)\ \text{kcal mol}^{-1}/RT)\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \quad \text{(VI)}$$

The respective preexponential factors found for the abstraction of fluorine atom from CF_3OF by radicals $CF_3OCHClCCl_2^{\bullet}$ [23] and $CF_3OCCl_2CCl_2^{\bullet}$ [24] were

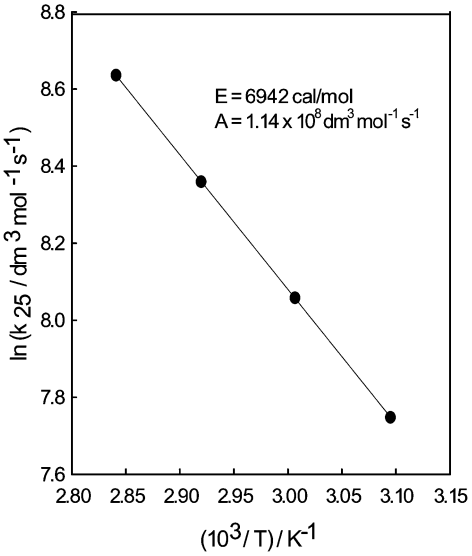

Figure 2 Arrhenius plot of rate constant k_{25}.

$(3.0 \pm 2) \times 10^9$ and $(3.7 \pm 0.5) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, and the corresponding activation energies were 5.62 ± 2.4 and 6.0 ± 1.1 kcal mol^{-1}, respectively.

As the termination rate $(k_{26}[R]^2)$ and k' are independent of temperature, the value of 6.95 kcal mol^{-1} for the activation energy E_{25} was obtained using the relation $E_{k'} = E_{25} - 0.5E_1 - 0.5E_{26}$, where $E_1 = 13.9$ kcal mol^{-1}, $E_{26} \approx 0$, and $E_{k'} \approx 0$.

The constants k at different temperatures were recalculated for each experiment, replacing $k_{25}(k_1k_{26})^{-0.5}$ in Eq. (IV) by the obtained value of k' and using rate constants k_1 calculated by Eq. (V). They are summarized in Table III.

The following mean values for k were obtained: $k_{(323.1\ K)} = (4.7 \pm 0.9) \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$, $k_{(332.6\ K)} = (9.4 \pm 1.9) \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$, $k_{(342.5\ K)} = (1.92 \pm 0.2) \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$, and $k_{(352.0\ K)} = (4.54 \pm 0.8) \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$.

DISCUSSION

The synthetic aspects of the thermal addition of CF_3OF to several haloalkenes have been reported by Johri and DesMarteau [25] and Sekiya and Ueda [26]. In their works the trifluoromethylhaloalkyl ethers were the main products. The observed reactivity and the low stereo- and regioselectivity indicated that these reactions occurred via a free-radical mechanism.

To investigate the kinetic and mechanistic aspects of the addition of CF_3OF to alkenes in the gas phase, the reactions of CF_3OF with C_3F_6 [27], C_4F_8 [22], CF_2CCl_2 [28], $CHClCCl_2$ [23], and CCl_2CCl_2 [24] in absence of O_2 and with CF_2CCl_2 [29], $CHClCCl_2$ [30], CCl_2CCl_2 [31], and C_3F_6 [32] in presence of O_2 have been studied.

The primary path in these gas-phase reactions is the homolytic cleavage of the O—F bond in a bimolecular reaction between CF_3OF and alkene (A), giving radicals $CF_3O^{\bullet}$ and $F(A)^{\bullet}$. The radicals $CF_3O^{\bullet}$ add rapidly to the double bond, forming $CF_3O(A)^{\bullet}$. The reaction of CF_3OF through the homolytic cleavage of its O—F bond was confirmed in the study of the addition of CF_3OF to a series of electron-poor haloalkenes (A) in a nonpolar solvent [33]. The $CF_3O(A)^{\bullet}$ intermediate radicals were observed by electron paramagnetic resonance and electron-nuclear double resonance techniques in the reaction systems CF_3OF + perfluoroalkenes [33,34]. It indicates that when the reactant–solvent interaction is weak, the gas-phase reaction dynamics rules may be carried over to the solution reactions [35], suggesting that, in this case, the mechanism valid for the liquid-phase reaction does not differ substantially from that for the gas-phase reaction.

Table III Constants k and $n = k/k_1$ at Different Temperatures

No. of Run	T (K)	Δt (min)	CF_3OF_i (Torr)	CF_3OF_f (Torr)	C_4F_{8i} (Torr)	C_4F_{8f} (Torr)	O_{2i} (Torr)	k (10^5 Torr^{-1} min^{-1})	n
26	323.1	303.9	19.8	16.4	97.8	88.8	81.3	1.44	2.25
27	323.1	237.0	12.0	10.4	89.3	85.5	81.1	1.39	2.17
28	323.1	449.8	11.5	10.5	58.8	54.1	51.5	1.37	2.14
2	332.6	27.0	23.6	22.4	94.8	92.8	270.4	2.75	2.39
3	332.6	358.6	14.6	6.4	204.8	183.6	154.8	2.60	2.26
4	332.6	226.2	13.0	9.0	100.3	92.7	99.1	2.71	2.36
22	332.6	123.3	19.5	16.5	100.5	93.6	102.0	2.66	2.31
23	332.6	124.0	13.4	8.8	302.4	289.5	153.6	2.89	2.51
24	332.6	191.0	8.5	5.3	198.9	191.3	150.6	2.70	2.35
6	342.5	188.0	14.2	8.6	100.6	84.6	118.0	5.33	2.60
7	342.5	181.3	11.7	5.5	202.5	184.3	149.8	5.44	2.65
8	342.5	298.5	6.5	2.0	200.6	186.2	150.6	5.39	2.63
9	342.5	187.0	20.0	16.8	48.7	37.9	77.5	5.47	2.67
10	342.5	130.0	19.7	15.1	102.2	88.0	106.9	5.48	2.67
11	342.5	239.4	4.8	3.1	88.0	83.3	100.6	5.30	2.59
12	352.0	134.8	11.0	7.0	102.4	86.4	111.6	12.1	3.50
13	352.0	70.5	19.1	14.9	100.9	84.7	113.6	12.0	3.47
14	352.0	170.8	11.3	8.7	51.2	38.9	69.2	12.9	3.73
15	352.0	195.4	6.5	3.4	102.1	89.0	101.7	12.6	3.64
16[a]	352.0	58.3	20.0	16.2	101.3	86.3	111.6	12.4	3.58
18	352.0	116.0	7.1	3.3	200.7	185.5	159.7	12.1	3.50
19	352.0	125.0	10.4	7.0	100.8	85.8	262.6	12.8	3.70
20[b]	352.0	59.8	19.9	16.0	101.5	86.3	109.0	12.4	3.58

Note: Δt is the reaction time. The subscripts i and f signify initial and final, respectively.

[a] 451.2 Torr of N_2 was present.

[b] The surface-to-volume ratio of the reaction vessel used in this experiment was 6.3 times greater.

In absence of O_2 the radicals $CF_3O(A)^{\bullet}$ abstract fluorine from CF_3OF, regenerating $CF_3O^{\bullet}$ and initiating the chain reaction with trifluoromethylhaloalkyl ethers, $CF_3O(A)F$, as the main products.

In presence of O_2 the radicals $CF_3O(A)^{\bullet}$ react rapidly with O_2, leading to the formation of haloalkoxy radicals $CF_3O(A)O^{\bullet}$, which initiate a series of reactions giving as the main products compounds containing the —C(O)X end group, where X = Cl or F.

The products formed in the gas-phase oxidation of C_3F_6, initiated by CF_3OF [32], are COF_2, $CF_3C(O)F$, $CF_3OC(O)F$, and a perfluorodiether, $CF_3OCF_2OCF_2C(O)F$.

At the temperature used in this work CF_3OF and perfluorobutene-2 are stable molecules and the reaction is homogeneous; thus it can be concluded that the primary process of this reaction is a bimolecular reaction between CF_3OF and C_4F_8, in which the homolytic cleavage of a rather weak bond O—F of CF_3OF occurs, generating $F(C_4F_8)^{\bullet}$ and $CF_3O^{\bullet}$ radicals. The $CF_3O^{\bullet}$ radicals add rapidly to the double bond of perfluorobutene, forming $CF_3O(C_4F_8)^{\bullet}$ radicals. The lack of formation of CF_3OOCF_3 confirms what was reported earlier, that the addition of $CF_3O^{\bullet}$ to the double bond of alkenes is considerably faster than any other reaction of $CF_3O^{\bullet}$ [36–41]. The values of the order of 10^{10} dm^3 mol^{-1} s^{-1} were determined for the addition of $CF_3O^{\bullet}$ to several alkenes [38–41].

The study of the equilibrium of $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$ [42] indicates that at the pressure of O_2 used in our work, the $CF_3O(C_4F_8)^{\bullet}$ radicals and other perfluoroalkyl radicals generated in this reaction system react rapidly with O_2. The high pressure limit values of 1.5×10^9 and 1.26×10^9 dm^3 mol^{-1} s^{-1} were reported for the rate constants for the O_2 addition to $CF_3^{\bullet}$ [43] and $CF_3CFHO^{\bullet}$ [44], respectively. The rate constants for the reactions of haloalkyl radicals with O_2 exceed those of fluorine atom abstraction from CF_3OF by several orders of magnitude [23,24,45,46]. Then the contribution of reaction (25) to the disappearance of CF_3OF and to the generation of $CF_3O^{\bullet}$ radicals must be very small, notwithstanding these few radicals contributing to initiate new chains. The CF_3OF is consumed principally by reaction (1). The amounts of CF_3OF consumed correspond closely to the calculated ones using k_1, the rate constant obtained previously for the gas-phase addition of CF_3OF to the double bond of C_4F_8 in absence of O_2 [22].

The lack of formation of perfluorobutene epoxide $CF_3CF\!-\!CFCF_3$ (O) indicates that the perfluoroalkyl

peroxy radicals do not add to the double bond at the conditions used in our work, disappearing preferentially by their self-reaction to give perfluoroalkoxy radicals. The available data for the addition of methyl peroxy radicals to alkenes [47], giving epoxy compounds as products, indicate that the rate constants for these additions are several orders of magnitude smaller than those for the self-reactions of peroxy radicals.

The perfuoroalkoxy radicals decompose via the C—C bond cleavage [48,49], this decomposition being the atmospheric fate of these radicals. The perfluoroalkoxy radicals containing ether groups and a relatively weak β-bond C—C in the —OCR_2—C(O)FCF_3 group, where R = F or CF_3, decompose principally by the β-scission, giving shorter perfluoroalkyl radicals and $CF_3C(O)F$ as products [2,3]. Rates of β-scission are determined by the stability of the radicals produced, depending on the nature and degree of substitution at the radical center [3,50]. It appears that the oxygen atoms attached to the adjacent carbon atoms in the C—C bond, as in the —OC—C(O) group of the $CF_3OCF(CF_3)C(O)^{\bullet}FCF_3$ radical, enhance the weakening of this bond, favoring β-scission (reaction (13)). In the study of the thermal gas-phase oxidation of C_3F_6, initiated by CF_3OF [32], it was found that the radical $CF_3OCF_2C(O)^{\bullet}FCF_3$, analogous to $CF_3OCF(CF_3)C(O)^{\bullet}FCF_3$, also decomposes principally by the β-scission of the C—C bond of the —OC—C(O) group, giving $R^{\bullet}$ and $CF_3C(O)F$ as products. The decomposition rates of fluorinated alkoxy radicals are very sensitive to change in molecular configuration. The $CF_3CF_2CFHO^{\bullet}$ radical decomposes 17 times more rapidly than the $CF_3CFHO^{\bullet}$ radical [51]. $CF_3CF_2CFHO^{\bullet}$ can be viewed as $CF_3CFHO^{\bullet}$ with one fluorine atom substituted by a CF_3 group.

Reaction (14) was proposed as an alternative route of decomposition of the radical $CF_3OCF(CF_3)C(O)^{\bullet}FCF_3$ by the α-scission, giving $CF_3^{\bullet}$ and $CF_3OCF(CF_3)C(O)F$, but it is not expected to occur to a great extent. No absorption bands that could be ascribed to $CF_3OCF(CF_3)C(O)F$ were observed in the IR spectra of the reaction products.

The cleavage of the O—C bond in the C—O—C ether group is not expected, as the activation energy for the scission of O—C bond in perfluorinated ethers is rather high, near 100 kcal mol^{-1} [52]. Then the principal route of decomposition of radicals $CF_3OC(O)^{\bullet}FCF_3$ (reaction (17)) and $CF_3CF_2OC(O)^{\bullet}FCF_3$ (reaction (24)) is the α-scission, giving $CF_3OC(O)F$ and $CF_3CF_2OC(O)F$, respectively, and radicals $CF_3^{\bullet}$, which reform the chain carriers $CF_3O^{\bullet}$.

The extrusion of the fluorine atom adjacent to the oxygen atom is unlikely because these processes are highly endothermic [53].

It appears that the amounts of $CF_3CF_2OC(O)F$ formed through reaction sequence (18)–(24) were too small to be detected, suggesting that in the temperature range used in this work, the thermal decomposition of $CF_3CF_2O^{\bullet}$ radical to give COF_2 and $CF_3^{\bullet}$ is more rapid than its addition to the double bond of perfluorobutene. It was found in the studies of oxidation of CF_3CF_2H (HFC-125) [54–56], in the study of the self-reaction of $CF_3CF_2O_2^{\bullet}$ radicals [57], and that of the reaction of $CF_3CF_2O_2^{\bullet}$ with NO [58], that the $CF_3CF_2O^{\bullet}$ radical was formed as a short-lived intermediate, whose fate was decomposition via C—C scission to give COF_2 and $CF_3^{\bullet}$. The rate constant value of 5.3×10^6 s^{-1} was calculated for the decomposition of $CF_3CF_2O^{\bullet}$ at 300 K [59]. It was also determined from the pulse radiolysis experiments at 296 K that $CF_3CF_2CF_2O^{\bullet}$ radicals decompose with a rate greater than 1.5×10^5 s^{-1} [48]. The decomposition rates of perfluoroalkoxy radicals increase with temperature.

The rate constant k_{25} was considered to be independent of the perfluoroalkyl radical structure. This supposition is supported by the room temperature values of the rate constants for the abstraction of a fluorine atom from CF_3OF by $CF_3^{\bullet}$ [45] and $C_2H_5^{\bullet}$ [46], reported to be 2×10^5 and $>6 \times 10^4$ dm^3 mol^{-1} s^{-1}.

Reaction (26) was proposed as chain termination. As no products of this reaction were detected, it indicates that in comparison with other products, only very small amounts of these compounds were formed.

The $CF_3O^{\bullet}$ radicals are generated by reaction (1), by the α C—C scission of perfluoroalkoxy radicals in presence of O_2, and by the abstraction of the fluorine atom from CF_3OF by $R^{\bullet}$.

CONCLUSION

Our work demonstrates the possibility of activating the complex mechanism of oxidation of fluorinated olefins with molecular oxygen by employing such a simple chemical initiator as CF_3OF, thus offering an alternative to UV radiation. It also shows that this singular oxidation mechanism has common characteristics as compared with those for the oxidation of fluoroolefins of different monomer structures. The efficiency of the initiator to produce perfluoroalkylpolyethers with controlled molecular mass depends on the competition between the rate of C—C bond scission of the perfluoroalkoxy radicals formed and their rate of addition to the olefin monomer. The lack of appreciable quantity of telomeric products containing ether group in the $CF_3OF + C_4F_8$-2 + O_2 system studied indicates that within the temperature and pressure range used in our

work, the principal route of disappearance of perfluoroalkoxy radicals $CF_3CF_2O^{\bullet}$ and $CF_3OC(O)^{\bullet}FCF_3$ is their decomposition giving $CF_3 + COF_2$ and $CF_3 + CF_3OC(O)F$, respectively.

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BIBLIOGRAPHY

1. Sianesi, D. ACS Polym Prepr 1971, 12, 411–419.
2. Sianesi, D.; Pasetti, A.; Fontanelli, R.; Bernardi, G. C.; Caporiccio, G. La Chimica e l'Industria 1973, 55, 208–221.
3. Faucitano, A.; Buttafava, A.; Comincioli, V.; Marchionni, G.; De Pascuale, R. J Phys Org Chem 1991, 4, 293–300.
4. Sianesi, D.; Marchionni, G.; De Pasquale, R. J. In Organic Fluorine Chemistry: Principles and Commercial Applications; Banks, R. E.; Smart, B. E.; Tatlow, J. C. (Eds.); Plenum: New York, 1994; pp. 431–461.
5. Bunyard, W. C.; Romack, T. J.; DeSimone, J. M. Macromolecules 1999, 32, 8224–8226.
6. Johnston, T.; Heicklen, J.; Stuckey, W. Can J Chem 1968, 46, 332–334.
7. Malavasi, M.; Sianesi, D. J Fluorine Chem 1999, 95, 19–25.
8. Sianesi, D.; Guarda, P. A.; Marchionni, G. Macromolecules 1999, 32, 7768–7780.
9. Rozen, S. Chem Rev 1996, 96, 1717–1736.
10. Czarnowski, J.; Castellano, E.; Schumacher, H. J. Z Phys Chem N F 1969, 65, 225–237.
11. Czarnowski, J.; Schumacher, H. J. Z Phys Chem N F 1970, 73, 68–76.
12. Kennedy, R. C.; Levy, J. B. J Phys Chem 1972, 76, 3480–3488.
13. Hohorts, F. A.; Shreeve, J. M. Inorg Synth 1967, 11, 143–146.
14. Nielsen, A. H.; Burke, T. G.; Woltz, P. J. H.; Jones, E. A. J Chem Phys 1952, 20, 596–604.
15. Loos, K. R.; Lord, R. C. Spectrochim Acta 1965, 21, 119–125.
16. Varetti, E.; Aymonino, P. J. J Mol Struct 1968, 1, 39–54.
17. Cutin, E. H.; Della Vedova, C. O.; Aymonino, P. J. An Asoc Quim Argent 1985, 73, 171–180.
18. Hermann, A.; Trautner, F.; Gholivand, K.; von Ahsen, S.; Varetti, E. L.; Della Vedova, C. O.; Willner, H.; Oberhammer, H. Inorg Chem 2001, 40, 3979–3985.
19. Arvia, A. J.; Aymonino, P. J. Spectrochim Acta 1962, 18, 1299–1309.
20. Durig, J. R.; Wertz, D. W. J Mol Spectrosc 1968, 25, 467–478.
21. Minkwitz, R.; Reinemann, S. Z Anor Allg Chem 1998, 624, 1695–1698.
22. dos Santos Afonso, M.; Schumacher, H. J. Z Phys Chem N F 1988, 158, 15–23.
23. Czarnowski, Z.; Czarnowski, J. J Chem Soc, Faraday Trans 1993, 89, 451–455.
24. Czarnowski, J. Int J Chem Kinet 1996, 28, 489–495.
25. Johri, K. K.; DesMarteau, D. D. J Org Chem 1983, 48, 242–250.
26. Sekiya, A.; Ueda, K. Chem Lett 1990, 609–612.
27. dos Santos Afonso, M.; Schumacher, H. J. Int J Chem Kinet 1984, 16, 103–115.
28. dos Santos Afonso, M.; Czarnowski, J. Z Phys Chem N F 1988, 158, 25–34.
29. Czarnowski, J. J Chem Soc, Faraday Trans 2 1989, 85, 1425–1437.
30. Czarnowski, J. Z Phys Chem N F 1995, 191, 103–118.
31. Czarnowski, J. Z Phys Chem N F 1998, 203, 183–197.
32. dos Santos Afonso, M.; Romano, R. M.; Della Vedova, C. O.; Czarnowski, J. Phys Chem Chem Phys 2000, 2, 1393–1399.
33. Navarrini, W.; Russo, A.; Tortelli, V. J Org Chem 1995, 60, 6441–6443.
34. Conti, F.; Corvaja, C.; Cremonese, F.; Navarrini, W.; Tortelli, V. J Chem Soc, Faraday Trans 1995, 91, 3813–3820.
35. Li, Y. S.; Wilson, K. R. J Chem Phys 1990, 93, 8821–8827.
36. Czarnowski, J. Int J Chem Kinet 1986, 18, 1323–1331.
37. Czarnowski, J. J Chem Soc, Faraday Trans 2 1987, 83, 579–586.
38. Chen, J.; Zhu, T.; Young, V.; Niki, H. J Phys Chem 1993, 97, 7174–7177.
39. Kelly, C.; Treacy, J.; Sidebottom, H. W.; Nielsen, O. J. Chem Phys Lett 1993, 207, 498–503.
40. Kelly, C.; Sidebottom, H. W.; Treacy, J.; Nielsen, O. J. Chem Phys Lett 1994, 218, 29–33.
41. Niki, H.; Chen, J.; Young, V. Res Chem Intermed 1994, 20, 277–301.
42. Knyazew, V.; Slagle, I. R. J Phys Chem A 1998, 102, 1770–1778.
43. Breheny, C.; Hancock, G.; Morrell, C. Z Phys Chem N F 2001, 215, 305–317.
44. Maricq, M. M.; Szente, J. J.; Kaiser, E. W. Chem Phys Lett 1992, 197, 149–156.
45. Shoikhet, A. A.; Teitelboim, M. A.; Vedeneev, V. I. Kinet Katal 1983, 24, 225–227.
46. Wang, N.; Rowland, F. S. J Chem Phys 1985, 89, 5154–5155.
47. Osborne, D. A.; Waddington, D. J. J Chem Soc, Perkin Trans II 1980, 925–930.
48. Giessing, A. M. B.; Feilberg, A.; Mogelberg, T. E.; Sehested, J.; Bilde, M.; Wallington, T. J.; Nielsen, O. J. J Phys Chem 1996, 100, 6572–6579.
49. Mogelberg, T. E.; Sehested, J.; Bilde, M.; Wallington, T. J.; Nielsen, O. J. J Phys Chem 1996, 100, 8882–8889.
50. Zhang, X. J Org Chem 1998, 63, 3590–3594.

51. Mogelberg, T. E.; Feilberg, A.; Giessing, A. M. B.; Sehested, J.; Bilde, M.; Wallington, T. J.; Nielsen, O. J. J Phys Chem 1995, 99, 17386–17393.
52. Waltman, R. J. J Fluorine Chem 1998, 90, 9–16.
53. Rayez, J. C.; Rayez, M. T.; Halvick, P.; Duguay, B.; Danneberg, J. J. Chem Phys 1987, 118, 265–272.
54. Edney, E. O.; Driscoll, D. J. Int J Chem Kinet 1992, 24, 1067–1081.
55. Tuazon, E. C.; Atkinson, R. J Atmos Chem 1993, 17, 179–199.
56. Hasson, A. S.; Moore, C. M.; Smith, I. W. M. J Chem Soc, Faraday Trans 1997, 93, 2693–2699.
57. Sehested, J.; Ellermann, T.; Nielsen, O. J.; Wallington, T. J.; Hurley, M. D. Int J Chem Kinet 1993, 25, 701–717.
58. Mogelberg, T. E.; Sehested, J.; Wallington, T. J.; Nielsen, O. J. Int J Chem Kinet 1997, 29, 209–217.
59. Sommitz, H.; Zellner, R. Phys Chem Chem Phys 2001, 3, 2352–2364.