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Kinetics and mechanism of thermal gas-phase oxidation of hexafluoropropene in the presence of trifluoromethylhypofluorite, CF₃OF

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The oxidation of hexafluoropropene with molecular oxygen in the presence of CF₃OF has been studied at 303.0, 313.0 and 323.4 K, using a conventional static system. The initial pressure of CF₃OF was varied between 1.7 and 16.6 Torr, that of C_3F_6 between 10.0 and 120.2 Torr and that of O_2 between 82.0 and 599.8 Torr. Several runs were made in the presence of 325.3-499.2 Torr of N_2 . Major products were COF₂, CF₃C(O)F, CF₃OC(O)F and a new compound, CF₃OCF₂OCF₂C(O)F. The latter was characterised by the determination of its relative molecular mass and its IR spectrum, which is consistent with the calculated one using theoretical approximations. Small amounts of CF₃OCF₂C(O)F were also formed. The oxidation is an homogeneous chain reaction, attaining, at the pressure of O_2 used, the pseudo-zero-order condition with respect to O_2 as a reactant. It is independent of the total pressure. The basic steps are: the thermal generation of CF₃O' radicals by abstraction of the fluorine atom from CF₃OF by C₃F₆, chain initiation by the addition of CF₃O' to olefin leading, in the presence of O_2 , to the formation of haloalkoxy radicals, which decompose *via* the C–C scission to give products containing C(O)F group and CF'₃ radicals, reforming CF₃O'. The full mechanism is postulated.

Introduction

During the last two decades fluorine chemistry has been continuously growing in terms of scientific contributions, as well as in the variety of innovative technologies and applications. Hypofluorite chemistry has led to the synthesis of a variety of new compounds with applications in many industrially important areas such as alternative refrigerants, pharmaceutical drugs, electronics, automotives, optics, aeronautical, membranes and coatings. The stable and easily handled trifluoromethylhypofluorite, CF₃OF, containing a weak O-F bond, is a versatile and selective fluorinating agent.¹ The value of 43.5 kcal mol⁻¹ for the dissociation energy of its O-F bond was determined by Czarnowski et al.² and, independently, by Kennedy and Levy.³ The thermal addition of CF₃OF 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 a synthetic and mechanistic point of view. It is expected that the field of fluoroxy compounds will continue to grow with benefits to organofluorine and general chemistry.

The synthetic aspects of thermal addition of CF_3OF to several haloalkenes (HA) have been reported by Johri and DesMarteau⁴ and Sekiya and Ueda.⁵ In their works the trifluoromethylhaloalkyl ether, $CF_3O(HA)F$, was formed as the main product. The observed reactivity and low stereo- and regioselectivity indicated that its formation occurred *via* a free radical mechanism.

The investigation of kinetic and mechanistic aspects of the additions of CF₃OF to haloalkenes was initiated by dos Santos Afonso and Schumacher, studying the thermal gasphase reactions of CF₃OF with C₃F₆⁶ and C₄F₈.⁷ It was followed by the studies of thermal reactions of CF₃OF with CF₂CCl₂,⁸ CHClCCl₂⁹ and CCl₂CCl₂¹⁰ in the absence of O₂ and those of the thermal oxidations of CF₂CCl₂,¹¹ CHClCCl₂¹² and CCl₂CCl₂¹³ initiated by addition of CF₃OF to the double bond.

In the above reactions of haloalkenes (HA) with CF_3OF , in the absence as well as in the presence of O_2 , two initial steps, common to both conditions, were postulated: the generation of CF_3O and F(HA) in the bimolecular reaction between CF_3OF and olefin and the addition of CF_3O to the double bond giving $CF_3O(HA)$. The elemental steps, postulated in these previous works, are referred to the analogue reactions in the reactions scheme for the oxidation of C_3F_6 , initiated by CF_3OF , summarised in Table 1.

$$CF_3OF + HA \rightarrow F(HA)' + CF_3O'$$

(see reactions (1) and (2), Table 1)

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Initiation (1) $CF_3OF + CF_3CF=CF_2 \rightarrow CF_3CF:CF_3 + CF_3O'$ (2) $CF_3OF + CF_3CF=CF_2CF_3CF_2C:F_2 + CF_3O'$ (2) $CF_3OF + CF_3CF=CF_2CF_3CF_2CF_2 + CF_3O'$ (3) $CF_3CFCF_3 + O_2 \rightarrow CF_3CF(O_2')CF_3$ (4) $CF_3CF(O_2')CF_3 + RO_2 \rightarrow CF_3CF(O')CF_3 + RO + O_2$ (5) $CF_3CF(O')CF_3 \rightarrow \underline{CF_3C(O)F} + CF_3'$ (6) $CF_3CF_2CF_2 + O_2 \rightarrow CF_3CF_2CF_2O_2'$ (7) $CF_3CF_2CF_2O_2' + RO_2 \rightarrow CF_3CF_2CF_2O' + RO + O_2$ (8) $CF_3CF_2CF_2O \rightarrow \underline{COF_2} + CF_3CF_2'$ (9) $CF_3CF_2O_2' + RO_2 \rightarrow CF_3CF_2O_2'$ (10) $CF_3CF_2O_2' + RO_2 \rightarrow CF_3CF_2O' + RO + O_2$ (11) $CF_3CF_2O' \rightarrow \underline{COF_2} + CF_3'$ Propagation (12) $CF_3 + O_2 \rightarrow CF_3O_2$ (13) $CF_3O_2 + RO_2 \rightarrow CF_3O' + RO + O_2$ (14) $CF_3O' + CF_3CF = CF_2 \rightarrow CF_3C'FCF_2OCF_3$ (15) $CF_3CFCF_2OCF_3 + \tilde{O}_2 \rightarrow CF_3CF(\tilde{O}_2)CF_2OCF_3$ (16) $CF_3CF(O_2)CF_2OCF_3 + RO_2 \rightarrow CF_3CF(O)CF_2OCF_3 + RO + O_2$ (17) $CF_3CF(O)CF_2OCF_3 \rightarrow \underline{CF_3CF(O)F} + CF_3OCF_2$ (18) $CF_3CF(O)CF_2OCF_3 \rightarrow \underline{CF_3CF(O)F} + CF_3$. (18) CF₃CF(0) CF₂OCF₃ \rightarrow CF₃OCF₂C(0)F + CF₃ (19) CF₃OCF₂O₂ \rightarrow OCF₃OCF₂O₂' (20) CF₃OCF₂O₂ \rightarrow CF₃OCF₂O' + RO + O₂ (21) CF₃OCF₂O' + CF₃CF=CF₂ \rightarrow CF₃OCF₂OCF₂C'FCF₃ (22) CF₃OCF₂OCF₂C;FCF₃ + O₂ \rightarrow CF₃OCF₂OCF₂CCF(O₂)CF₃ (23) CF₃OCF₂OCF₂C;F(O₂)CF₃ + RO₂ \rightarrow CF₃OCF₂OCF₂CCF(O₂)CF₃ + RO + O₂ (24) CF₃OCF₂OCF₂C;F(O))CF₃ \rightarrow CF₃OCF₂OCF₂C(O)F + CF₃' (25) CF O' + CF CF=CF \rightarrow CF CFOCF O' F (25) $CF_3O' + CF_3CF = CF_2 \rightarrow CF_3\overline{CF(OCF_3)C'F}$ (26) $CF_3CF(OCF_3)CF_2 + O_2 \rightarrow CF_3CF(OCF_3)CF_2O_2$ $\begin{array}{l} (20) \ CF_3CF(OCF_3)CF_2+O_2\rightarrow CF_3CF(OCF_3)CF_2O_2\\ (27) \ CF_3CF(OCF_3)CF_2O_2+RO_2\rightarrow CF_3CF(OCF_3)CF_2O^*+RO+O_2\\ (28) \ CF_3CF(OCF_3)CF_2O^*\rightarrow CF_3CF(OCF_3)+\frac{COF_2}{2}\\ (29) \ CF_3CFOCF_3+O_2\rightarrow CF_3CF(O_2)OCF_3\\ (30) \ CF_3CF(O_2)OCF_3+RO_2\rightarrow CF_3CF(O^*)OCF_3+RO+O_2\\ (31) \ CF_3CF(O^*)OCF_3\rightarrow \underline{CF_3OC(O)F}+CF_3\\ \end{array}$ Termination (32) $CF_3O' + CF_3O' \rightarrow CF_3OOCF_3$ (33) $CF_3OCF_2O' + CF_3OCF_2O' \rightarrow CF_3OCF_2OOCF_2OCF_3$

^{*a*} RO₂ = CF₃CF(O₂)[.]CF₃, CF₃CF₂CF₂O₂[.], CF₃CF₂O₂[.], CF₃O₂[.], CF₃CF(O₂)[.]CF₂OCF₃, CF₃OCF₂O₂[.], CF₃OCF₂OCF₂CF(O₂)[.]CF₃, CF₃CF(OCF₃)CF₂O₂[.], CF₃CF(O₂)[.]OCF₃ and RO = CF₃CF(O)[.]CF₃, CF₃CF₂CF₂O[.], CF₃CF₂O[.], CF₃CF(O)[.]CF₃CF(O)[.]CF₂OCF₃, CF₃OCF₂O[.], CF₃CF(O)[.]CF₃CF(O)[.]CF₂OCF₃, CF₃OCF₂O[.], CF₃CF(O)[.]CF₃CF(O)[.]CF₃CF(O)[.]CF₃OCF₂O[.], CF₃CF(O)[.]CF(O)[.]CF(O)[.]CF(O)[.]CF(O)[.]CF(O)[.]CF(O)[.]CF(O)[.]CF(O

 $CF_3O' + HA \rightarrow CF_3O(HA)'$

(see reactions (14) and (25), Table 1)

In the absence of O_2 the CF₃O(HA)^{\cdot} radical abstracts the fluorine atom from CF₃OF, accompanied by the simultaneous formation of another CF₃O' radical, initiating a chain reaction with trifluoromethylhaloalkyl ether as the main product.

$$CF_3O(HA)$$
 + $CF_3OF \rightarrow CF_3O(HA)F + CF_3O$

In the presence of O₂, the CF₃O(HA)[•] radicals react rapidly with O₂, leading to the formation of haloalkoxy radicals:

$$CF_3O(HA)' + O_2 \rightarrow CF_3O(HA)O_2'$$

(see reactions (15) and (26), Table 1)

$$2CF_3O(HA)O_2 \rightarrow 2CF_3O(HA)O' + O_2$$

(see reactions (16) and (27), Table 1)

The principal way of decomposition of CF₃O(HA)O⁻ haloalkoxy radicals, where $HA = CF_2CCl_2$, $CHClCCl_2$ and CCl₂CCl₂, is the detachment of Cl⁻ for the CCl₂O group. The chlorine atoms add to CX_2CCl_2 , where X = H, Cl or F, initiating, in the presence of O₂, a chain reaction with Cl as chain carriers and CX₂ClC(O)Cl as the main products.

In recent studies of the reactions of CF₃OF with C₃F₆ and other haloalkenes in a non-polar solvent, the formation of the F(HA)' and CF₃O(HA)' intermediate radicals was observed using EPR and ENDOR techniques and CF₃O(HA)F was detected as the product.^{14,15} It indicates that, when the reactant-solvent interaction is weak, the gas-phase reaction

dynamics rules may be carried over to the solution reactions.16

The photooxidation of C₃F₆ by molecular O₂ was studied in the condensed phase at 233 K,¹⁷ using a high-pressure mercury lamp. It was found that the reaction is a complex free-radical process, leading to the formation of perfluoro and polyperfluoro ethers and products containing the C(O)F group, but the full reaction scheme has not been clarified.

The perfluoro ethers are proposed as alternative refrigerants and polyperfluoro ethers are used as lubricants in the magnetic recording industry.

In this work the study of the thermal gas-phase oxidation of C_3F_6 , initiated by the addition of CF_3OF to the double bond, has been undertaken in order to elucidate the elementary steps involved in this system and to characterise the final reaction products.

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 cm³ (S/V = 0.75 cm⁻¹) and another one of similar dimension filled with small pieces of quartz tubing (S/ $V = 4.7 \text{ cm}^{-1}$). 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 Perkin-Elmer 325 and Perkin-Elmer 1600 Series FTIR spectrometers, using 10 cm cells provided with NaCl and KBr

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.¹⁸ C₃F₆ (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. O₂ (La Oxigena, 99.99%) and N₂ (La Oxigena, 99.9%) were bubbled through 98% analytical-grade H₂SO₄, and passed slowly through a Pyrex coil at 123 K and at liquid air temperature, respectively.

The reaction was followed measuring the pressure decrease as a function of time. The experiments were made at 303.0, 313.0 and 323.4 K. The initial pressure of CF₃OF was varied between 1.7 and 16.6 Torr, that of C_3F_6 between 10.0 and 120.2 Torr and that of O_2 between 82.0 and 599.8 Torr. Several runs were carried out in the presence of N₂, varying its pressure from 325.3 to 499.2 Torr. Two experiments were made in the reactor with S/V = 4.7 cm⁻¹.

Results

The reaction is an homogeneous chain reaction, independent of the total pressure. At the pressure of O_2 used in this work, the reaction attained the pseudo-zero-order condition with respect to O_2 as a reactant.

Within the temperature range of this work, and in the absence of CF_3OF , no reaction was observed between per-fluoropropene and O_2 after several hours.

In the presence of CF_3OF , three products were detected by means of infrared spectroscopy, COF_2 ,¹⁹ $CF_3C(O)F^{20}$ and $CF_3OC(O)F$.^{21,22} The formation of an unknown compound was also observed. According to the experimental evidence, supported by theoretical findings, the structure of $CF_3OCF_2OCF_2C(O)F$ has been assigned to this compound. Its infrared spectrum, shown in Fig. 1, compares well with the calculated one for this molecule, using the HF/3-21G* approximation. It is discussed in more details in the Theoretical calculations section. The proposed composition is consis-



Fig. 1 FTIR spectrum of $CF_3OCF_2OCF_2C(O)F$ at room temperature: pressure 2.5 Torr, optical path 10 cm, resolution 1 cm⁻¹.

tent with the relative molecular mass of 244 ± 6 determined for this compound by gas-density measurements with a calibrated Pyrex bulb (theoretical relative molecular mass of CF₃OCF₂OCF₂C(O)F is 248). No data on CF₃OCF₂OCF₂C(O)F were found in the literature. The absorption band at 1550 cm⁻¹ characteristic of the epoxy group of hexafluoropropene oxide was not observed in the infrared spectra.

All experiments were carried out until the complete consumption of C_3F_6 . For analysing the reaction mixture of each experiment, the reaction vessel was rapidly cooled to liquid air temperature and the mixture separated by fraction condensation. Any N2, if present, and non-consumed O2 were separated as volatile at liquid air temperature as the first fraction, Fr1. The second fraction, Fr2, volatile at 123 K, consisted of CF₃OF and COF₂. The third fraction, Fr₃, volatile at 163 K, was composed of CF₃C(O)F and CF₃OC(O)F. To determine the concentration of COF_2 in Fr_2 and that of $CF_3OC(O)F$ in Fr_3 , infrared calibration curves were constructed using pure compounds, thereby allowing conversion of the absorption intensities at 1942 and 1028 cm⁻¹ to the pressure of COF₂ and CF₃OC(O)F, respectively. The amounts of CF_3OF and $CF_3C(O)F$ in the corresponding fractions Fr_2 and Fr3 were obtained by difference. The compound $CF_3OCF_2OCF_2C(O)F$ remained as a residue at 163 K.

The analytical data of 6 experiments are summarised in Table 2. In this table, subscripts i and f signify initial and final. From these data the following can be deduced: The consumption of CF₃OF was <1%. The concentrations of COF₂ and CF₃OC(O)F formed were equal to those of CF₃C(O)F and CF₃OCF₂OCF₂C(O)F, respectively. The final pressure decrease of each run, Δp , was equal to the sum of the following products: [CF₃C(O)F] + [CF₃OCF₂OCF₂C(O)F] +0.5[COF₂]. The amount of O₂ consumed in each run was equal to the sum of [CF₃C(O)F] + [CF₃OCF₂OCF₂C(O)F] +0.5([COF₂] + [CF₃OC(O)F]). The sum of the products: [CF₃C(O)F] + [CF₃OCF₂OCF₂C(O)F] + 0.5([COF₂] + [CF₃OC(O)F]], was approximately equal to 98.5% [C₃F₆]_i.

Discussion

Johri and DesMarteau showed in their study of reactivity of CF_3OF with some haloalkenes in the condensed phase, that these reactions occur *via* a free radical mechanism consistent with the observed reactivity and low stereo- and regioselectivity.⁴

The basic steps postulated to explain the experimental results of our kinetic and mechanistic studies of the thermal gas-phase reactions of CF₃OF with C_3F_6 , 6C_4F_8 , 7CF_2CCl_2 , 8CHClCCl_2 ⁹ and CCl_2CCl_2 ¹⁰ in the absence of O₂ and those of the oxidations of CF₂CCl₂, 11 CHClCCl₂¹² and CCl₂CCl₂¹³ initiated by addition of CF₃OF to the double bond, were: 1. The generation of CF₃O and F(HA) radicals in the bimolecular reaction between CF₃OF and the olefin. 2. The addition of CF₃O' to the double bond generating CF₃O(HA) radicals. 3. The abstraction of fluorine atom from

Table 2 Analytical data of 6 experiments carried out to the total consumption of $C_3 F_6^{a}$

Run	T/K	Δp /Torr	CF ₃ OF _i /Torr	C ₃ F _{6i} /Torr	O _{2i} /Torr	Fr ₂ /Torr	COF _{2f} /Torr	Fr ₃ /Torr	CF ₃ OC(O)F /Torr	CF ₃ OCF ₂ OCF ₂ C(O)F /Torr	O _{2f} /Torr
8	303.0	25.1	3.5	30.6	294.9	13.7	10.3	20.4	10.4	9.8	259.7
12	313.0	24.1	3.2	29.4	102.0	12.8	9.8	19.5	9.8	9.5	86.4
15	313.0	50.2	5.0	61.2	121.6	24.2	19.6	40.0	19.7	20.5	51.7
16	313.0	13.4	4.2	16.4	106.1	10.1	6.0	11.1	6.1	5.1	87.1
18	323.4	8.2	2.6	10.0	96.6	6.3	3.8	6.9	3.8	2.9	85.1
19	323.4	24.5	2.6	29.9	99.3	13.5	11.1	20.1	10.9	9.3	64.9
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 $\operatorname{Fr}_2 = [\operatorname{CF}_3\operatorname{OF}] + [\operatorname{COF}_2] \text{ and } \operatorname{Fr}_3 = [\operatorname{CF}_3\operatorname{OC}(\operatorname{O})\operatorname{F}] + [\operatorname{CF}_3\operatorname{C}(\operatorname{O})\operatorname{F}].$

CF₃OF by CF₃O(HA)', giving CF₃O' as chain carriers and CF₃O(HA)F as the main products in the absence of O₂; (4) the rapid reaction of CF₃O(HA)' radicals, where HA = CX_2CCl_2 and X = H, Cl or F, with O₂, leading to the formation of haloalkoxy radicals and CX₂ClC(O)Cl as the main products in the presence of O₂.

It is well known that the principal way of disappearance of haloalkoxy radicals, containing an oxygen atom attached to the CCl_2 group, is the detachment of chlorine atoms. The addition of the chlorine atoms to CX_2CCl_2 in the presence of oxygen leads to the chain formation of CX_2ClCCl_2O radicals that decompose reforming Cl and giving $CX_2ClC(O)Cl$.

Recently the radical mechanism was strongly reinforced by the work of Navarrini et al. who studied the kinetics of the addition of CF₃OF to a series of electron poor haloalkenes in a non-polar solvent in the absence of O_2 .¹⁵ They determined the relative rate constants of the initiation, chain-propagation and termination steps. The final products were $CF_3O(HA)F$. Their work clearly concluded that CF₃OF reacts through the homolytic cleavage of its O-F bond. The ultimate proof for the existence of a free radical mechanism was the observation of F(HA)' and CF₃O(HA)' intermediate radicals by EPR and ENDOR techniques in the reaction system CF₃OF + perfluoroalkenes.¹⁴ It indicates that, when the reactantsolvent interaction is weak, the gas-phase reaction dynamics rules may be carried over to the solution reactions,¹⁶ suggesting that in this case the mechanism for the liquid-phase reaction does not differ substantially from that for the gas-phase reaction.

In order to propose a reaction mechanism for the gas-phase oxidation of C_3F_6 in the presence of CF_3OF , the above considerations were taken into account. The mechanism presented in Table 1 explains well the experimental results obtained in our work.

At temperatures of this work CF₃OF and C₃F₆ are stable molecules and the reaction is homogeneous, thus it can be concluded that the primary process of this reaction is the bimolecular reaction between CF₃OF with C₃F₆, generating F(C₃F₆)⁻ and CF₃O⁻ radicals. The CF₃O⁻ radicals react rapidly with perfluoropropene, forming CF₃O(C₃F₆)⁻ radicals. It was reported that the addition of CF₃O⁻ to the double bond of alkenes is considerably faster than any other reaction of CF₃O⁻,²³⁻²⁸ the values of the corresponding rate constants being of the order of 10¹⁰ dm³ mol⁻¹ s⁻¹ for the addition of CF₃O⁻ to several alkenes.²⁵⁻²⁸ The compounds CF₃OCF₂CF₂CF₃ and CF₃OCF(CF₃)₂ were reported as products of the reaction of CF₃O⁻ with CF₃CF=CF₂ in the condensed phase and in the absence of O₂,⁴ indicating that the addition of CF₃O⁻ radicals to the double bond of hexafluoropropene proceeds *via* two channels: addition to α and β carbon, respectively.

The equilibrium study of $\mathbb{R}^{\cdot} + \mathbb{O}_2 \leftrightarrow \mathbb{RO}_2^{\cdot 2^9}$ indicates that at the pressure of \mathbb{O}_2 used in this work, the perfluoro alkyl radicals react rapidly with \mathbb{O}_2 . The rate constants for haloalkyl radicals with \mathbb{O}_2 exceed those of fluorine atom abstraction from CF₃OF by three or four orders of magnitude.^{30,31} The lack of formation of hexafluoropropene oxide indicates that perfluorinated peroxy radicals do not add to the double bond, disappearing by their self-reaction to give perfluoroalkoxy radicals. The available data for the additions of methyl peroxy radicals to alkenes,³² giving epoxy compounds as products, indicate that the rate constants for these additions were several order of magnitude smaller than those for the self-reactions of peroxy radicals.

By analogy to other perfluoroalkoxy radicals,^{33,34} the perfluoroalkoxy radicals, containing the ether group, decompose via the C–C bond scission, generating, through a sequence of reactions, compounds containing the C(O)F group and CF₃ radicals, which reform the CF₃O' chain carriers. The scission of C–O bond in the C–O–C ether group in CF₃O(C₃F₆)O', CF_3OCF_2 and CF_3OCF_2O' radicals is not expected, as the activation energy for the cleavage of the C–O group in perfluorinated ethers is rather high, near 100 kcal mol^{-1,35} The extrusion of fluorine atom adjacent to oxygen atom in perfluoroalkoxy radicals is unlikely for these processes are highly endothermic.³⁶

As during the reaction course the consumption of CF_3OF was <1%, the production of $CF_3C(O)F$ and COF_2 through reactions (5), (8) and (11) is very small in comparison with the chain formation of these products.

Reaction (18) was proposed as an alternative route of decomposition of the CF₃C(O')FCF₂OCF₃ radical, giving $CF_3OCF_2C(O)F$ and the CF_3 radical. Comparison of the infrared spectrum of $CF_3OCF_2C(O)F^{37}$ with that obtained in this work, indicates that, relative to other products, only small amounts of this product have been formed. This is confirmed by the yields of the major products: $[CF_3C(O)F] +$ $[CF_3OCF_2OCF_2C(O)F] + 0.5([COF_2] + [CF_3OC(O)F]) \approx$ 98.5% $[C_3F_6]$. It indicates that reaction (17) is more rapid than reaction (18), suggesting that oxygen atoms attached to each of the adjacent carbon atoms in the C-C bond, as in the $O-C-C-(O)-CF_3$ group of the $CF_3CF(O)CF_2OCF_3$ radical, enhance the weakening of this C-C bond. Reaction (17) was postulated to explain the reported formation of $CF_3C(O)F$ in condensed-phase photooxidation of C_3F_6 .¹⁷ Rates of β scission are partially determined by the stability of radicals produced, depending on the nature and degree of substitution at the radical centre.^{17,38} It appears that the introduction of the CF_3OCF_2O group replacing the CF_3O group on the γ carbon in the CF₃OCF₂OCF₂CF(O')CF₃ radical favours the α scission by inductive effect.

The addition of such a bulky radical as CF_3OCF_2O' to the β -carbon of C_3F_6 was considered, but it was not included in the mechanism, assuming that the rate of this addition would be much lower that the rate of reaction (21).

Reactions (32) and (33) were proposed as chain termination reactions. No products of these reactions were detected. It indicates that, in comparison to the long-chain products, only very small amounts of these compounds were formed. In the reaction of CF₃OF with C₃F₆, in absence of O₂,⁶ where CF₃O[•] was generated as a chain carrier by the abstraction of fluorine atom from CF₃OF by CF₃O(HA)[•], small amounts of CF₃OOCF₃ were observed by its characteristic absorption band at 1166 cm⁻¹ in the infrared spectra of final reaction mixtures of experiments where [CF₃OF] > [C₃F₆].

The CF₃O[•] radicals generated from CF₃OF through reactions (1) and (2) initiate chains with CF₃O[•] and CF₃OCF₂O[•] radicals, originated by the C–C bond scission of per-fluoroalkoxy radicals, as the chain carriers.

Applying the steady-state approximation to this mechamism the following expression was obtained for the consumption of perfluoropropene:

$$- d[C_{3}F_{6}]/dt$$

$$= (k_{1} + k_{2})[CF_{3}OF][C_{3}F_{6}]$$

$$+ (k_{14} + k_{25})[(k_{1} + k_{2})/2k_{32}]^{0.5}[CF_{3}OF]^{0.5}[C_{3}F_{6}]^{1.5}$$

$$+ k_{21}(k_{14}/2k_{33})^{0.5}[(k_{1} + k_{2})/2k_{32}]^{0.25}$$

$$\times [CF_{3}OF]^{0.25}[C_{3}F_{6}]^{1.75} \qquad (I)$$

The kinetic chain length, the ratio between the consumption rate of C_3F_6 and the rate of initiation, $(k_1 + k_2)[CF_3OF]_i$ [C_3F_6]_i may be written as follows:

$$CL = 1 + \lambda [([C_3F_6]/[CF_3OF])/([C_3F_6]_i/[CF_3OF]_i)]^{0.25}$$
(II)

where the subscript i denotes initial concentrations of reactants. The initial chain length for each experiment is:

$$CL_i = 1 + \lambda$$
 (III)

where

$$\lambda = \{ [(k_{14} + k_{25})[CF_3O^{-}] + k_{21}[CF_3OCF_2O^{-}]][C_3F_6]_i \} / (2k_{32}[CF_3O^{-}]^2)$$
(IV)

 λ is the chain length of a special type of the chain reaction, which propagates by chain carriers generated and successively reformed by the scission of the C-C bond of perfluoroalkoxy radicals. The values of λ obtained, as described in the following section, show that λ is independent of the temperature, the ratio of propagation rate to that of termination being practically constant. As the termination rate does not depend on temperature, it follows that the propagation rate is also temperature independent. Assuming that k_{32} is equal to the collisional factor, 10^{10} dm³ mol⁻¹ s⁻¹, it indicates that the activation energies E_A for the addition of perfluoroalkoxy radicals to the double bond of perfluorinated alkenes must be very small: $E_{A14} \approx E_{A21} \approx E_{A25} \approx 0$. The reported rate constants for the addition of CF₃O to alkenes are of the order of 10^{10} dm³ mol⁻¹ s⁻¹.²⁵⁻²⁸ The behaviour of λ also suggests, that the activation energy for the rupture of the C-C bond in perfluoroalkoxy radicals to give CF₃O' and CF₃OCF₂O' in the presence of O2 must be very small, the rate constant for the formation of these chain carriers being practically independent of the temperature. It was determined from the pulse radiolysis experiments at 296 K that CF₃CF₂CF₂O radicals decompose with a rate greater than 1.5×10^5 s⁻¹.³³ The atmospheric fate of the CF₃CF₂CF₂O^{.33} and $CF_3CF(O)CF_3$ ³⁴ radicals is the C-C bond scission.

Data treatment

 λ was determined as a slope, plotting $CL_{exp} - 1$ as a function of {([C₃F₆]/[CF₃OF])/([C₃F₆]_i/[CF₃OF]_i)}^{0.25}. The CL_{exp} is the experimental chain length equal to $V_{exp}/(k_1 + k_2)$ [CF₃OF][C₃F₆], where V_{exp} is:

$$-d[C_3F_6]/dt =$$

1

$$\{1 + \lambda [([C_3F_6]/[CF_3OF])/([C_3F_6]_i/[CF_3OF]_i)]^{0.25} \} \\ \times (k_1 + k_2) [CF_3OF][C_3F_6]$$
(V)

Plots at 303.0, 313.0 and 323.4 K are illustrated in Figs. 2-4, respectively.

The sum of the constants $k_1 + k_2$ was calculated by the following expression obtained previously:⁶

$$x_{1} + k_{2} = 7.6 \pm 0.68 \times 10^{8} \times \exp(-15.9 \pm 0.45 \text{ kcal/}RT) \text{dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$

$$x \exp(-15.9 \pm 0.45 \text{ kcal/}RT) \text{dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$

$$x \exp(-15.9 \pm 0.45 \text{ kcal/}RT) \text{dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$

$$R^{2} = 0.9837$$

Fig. 2 The plot of $(CL_{exp} - 1)$ vs. $\{([C_3F_6]/[CF_3OF])/([C_3F_6], [CF_3OF])\}^{0.25}$ at 303.0 K, where $CL_{exp} = experimental chain length = <math>V_{exp}/(k_1 + k_2)[CF_3OF][C_3F_6]$. The value of the slope, equal to λ , is given in the Table 3.

{([C₃F₆]/[CF₃OF])/([C₃F₆]/[CF₃OF]_i)}^{0.25}



Fig. 3 The plot of $(CL_{exp} - 1)$ vs. $\{([C_3F_6]/[CF_3OF])/([C_3F_6]_i/[CF_3OF]_i)\}^{0.25}$ at 313.0 K, where $CL_{exp} = experimental chain length = <math>V_{exp}/(k_1 + k_2)[CF_3OF][C_3F_6]$. The value of the slope, equal to λ , is given in the Table 3.

The values of λ and those of $k_1 + k_2$ at different temperatures are given in Table 3. In the temperature range studied, λ is equal to 184.2 and does not depend on the initial pressure of each experiment.

The results of 16 experiments[†] illustrate the good agreement between the experimental rate of consumption of C_3F_6 , $V_{exp} = R(\Delta p/\Delta t)$, and V_{cal} , the rate of consumption of C_3F_6 ,



Fig. 4 The plot of $(CL_{exp} - 1)$ vs. $\{([C_3F_6]/[CF_3OF])/(CF_3OF])/([C_3F_6]_i/[CF_3OF]_i)\}^{0.25}$ at 323.4 K, where CL_{exp} = experimental chain length = $V_{exp}/(k_1 + k_2)[CF_3OF][C_3F_6]$. The value of the slope, equal to λ , is given in the Table 3.

Table 3 Constants $(k_1 + k_2)$ for the addition of CF₃OF to the double bond of C₃F₆ and $\lambda = CL_i - 1$, where CL_i is the initial chain length of each experiment, at different temperatures

T/K	$k_1/10^{-5} \text{ Torr}^{-1} \min^{-1}$	λ
303.0	0.835	184.1
313.0	1.880	184.2
323.4	4.135	184.3

† Available as electronic supplementary information. See http:// www.rsc.org/suppdata/cp/a9/a908989f

Table 4 Calculated energies for the gauche and cis conformers of $CF_3OCF_2OCF_2C(O)F$

Approximation	Egauche/Hartrees	E _{cis} /Hartrees	$\Delta E (E_{cis} - E_{gauche})/\text{kcal mol}^{-1}$
HF/3-21G*		-1165.2246511	0.97
B3LYP/6-31 + G*		-863.851952905	0.19

calculated by eqn. (V) and show the experimental chain lengths $CL_{exp} = V_{exp}/(k_1 + k_2)[CF_3OF][C_3F_6]$. Δp is the pressure decrease, Δt the reaction time and R is equal to $[C_3F_6]_i/\Delta p_f$. The subscripts i and f signify initial and final. The amounts of C_3F_6 consumed, corresponding to Δp , were calculated, point by point, multiplying Δp by R. The amounts of CF_3OF consumed at $\Delta t = t_n - t_{n-1}$ were computed, point by point, by $[CF_3OF]_n\{1 - exp[-(k_1 + k_2)\Delta t[C_3F_6]_m]\}$, where n = 1, 2, 3, ... n and $[C_3F_6]_m$ is the mean pressure of C_3F_6 in the interval Δt .

Theoretical calculations

In order to compare the experimental vibrational data of the obtained unknown compound with the proposed one, $CF_3OCF_2OCF_2C(O)F$ was theoretically studied with *ab initio* and density functional theory methods.

All calculations were performed using the GAUSSIAN 94 program system³⁹ under a Linux environment on a personal computer. First, the electronic energy surface was investigated. using the HF/3-21G* and B3LYP/6-31 + G* levels of theory. Two stable conformers were found, as depicted in Fig. 5. The first conformer presents the C(1)-O(2) bond gauche with respect to the C(4)-O(5) bond and the C(1)-F(3) bond staggered between the C(4)-F(6) and the C(4)-O(5) bonds. The second conformer with the C(1)-O(2) bond *cis* with respect to the C(4)–O(5) and the C(1)–F(3) bond staggered between the C(4)-F(6) and C(4)-F(7) bonds. These structures are in agreement with the expected ones for compounds of the type RCC(O)X.40 Energy minima with respect to nuclear coordinates for which no imaginary wavenumbers occur were obtained by simultaneous relaxation of all geometric parameters for the two conformers depicted in Fig. 5. Energy differences calculated for the two forms with the HF/3-21G* and $B3LYP/6-31 + G^*$ levels of the theory are listed in Table 4. The gauche conformer is predicted by both approximations as the most stable form.

Table 5 lists vibrational wavenumbers of two conformers of $CF_3OCF_2OCF_2C(O)F$ calculated using the $HF/3-21G^*$ approximation, together with the experimental IR wavenumber values obtained for the unknown compound, correspond-

Fig. 5 Molecular models of the two conformers of $CF_3OCF_2OCF_2C(O)F$ calculated with the B3LYP/6-31 + G* approximation.

ing to the spectrum depicted in Fig. 1. Calculated values are scaled by the 0.9 factor, due to the known overestimation of the wavenumbers by *ab initio* methods in the Hartree–Fock approximation. Theoretical results are in good agreement with experimental values.

 $CF_3OCF_2(O)F$ was also investigated because of the following reasons: the formation of this compound during the thermal-reaction was postulated and was found consistent with the experimental results. Its known IR spectrum allows comparison with the theoretical data obtained for this compound using the same procedure that was employed for $CF_3OCF_2OCF_2(O)F$ thus confirming the reliability of the

Table 5 Calculated wavenumbers of the gauche and cis conformersof $CF_3OCF_2OCF_2C(O)F$ using the HF/3-21G* approximation andexperimental values corresponding to the spectrum depicted in Fig. 1

$\frac{Gauche}{v/cm^{-1a}}$ conformer	Cis conformer v/cm^{-1a}	Experimental ν/cm^{-1}		
		1959		
1887	1892	1898		
1393	1393	1070		
1347	1342			
1330	1323	1317		
1330	1220	1284		
1295	1209	1204		
1290	1205			
1200	1273	1250		
1230	1237	1230		
1229	1217	11/4		
1181	1199	114/		
1116	1119	1125		
		1104		
0.40	0.40	1028		
948	948	952		
		906		
819	814			
793	793			
770	749	769		
719	732	716		
672	687	690		
641	645			
613	618	618		
570	576			
545	555			
542	537			
497	497			
478	479			
441	408			
364	384			
349	337			
334	319			
306	303			
253	242			
212	226			
189	197			
148	149			
96	96			
62	62			
58	47			
43	37			
35	37			
35 26	32 25			
20	23			
^a Scaled by a factor of 0.9.				



Table 6 Calculated wavenumbers of the *gauche* and *cis* conformers of $CF_3OCF_2C(O)F$ using the HF/3-21G* approximation and experimental values (ref. 37)

Gauche conformer v/cm^{-1a}	Cis conformer v/cm^{-1a}	Experimental ³⁷ ν/cm^{-1}			
1886	1892	1893			
1381	1379				
1339	1338	1340			
1320	1300				
1270	1253	1280			
1237	1239	1247			
1198	1215	1198			
		1145			
1123	1123	1092			
		925			
		910			
886	881	831			
795	792	760			
737	738	732			
708	704	700			
618	629				
599	615				
561	586				
518	502				
489	480				
429	408				
355	349				
329	329				
322	307				
215	227				
194	205				
115	112				
59	57				
51	39				
32	31				
^{<i>a</i>} Scaled by a factor of 0.9.					

results obtained. Calculations for $CF_3OCF_2C(O)F$ were performed using HF/3-21G* and B3LYP/6-31+G* approximations. In Table 6 the theoretical vibrational results calculated with HF/3-2G* approximations for two conformers (*gauche* and *cis*) are presented. Experimental wavenumbers reported by Schack and Christe³⁷ are also included.

Theoretical vibrational spectra of $CF_3OCF_2OCF_2C(O)F$ and $CF_3OCF_2C(O)F$ are, as expected, very similar. The calculated spectrum of the proposed new and unknown compound is in good agreement with experimental results. According to this evidence and taking into account its molecular mass determined by gas-density measurements the formation of $CF_3OCF_2OCF_2C(O)F$ was thus proposed. Experiments to obtain a larger quantity of this compound and to complete its analysis are currently being carried out in our laboratory.

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