

THERMAL GAS-PHASE OXIDATION OF TRIFLUOROBROMOETHENE, CF_2CFBr , INITIATED BY NO_2

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Dedicated to the memory of the late Prof. Hans J. Schumacher
on the occasion of his 100th birthday

Abstract

The oxidation of CF_2CFBr by molecular O_2 initiated by the addition of NO_2 to the double bond of the alkene was studied at 313.4 K, using a conventional static system. The initial pressure of CF_2CFBr was varied between 18.8 and 43.9 torr; that of NO_2 between 0.9 and 4.8 torr and that of O_2 between 96.9 and 402.9 torr. The following products were formed: $CF_2BrC(O)F$, as the main product, $C(O)F_2$ and $C(O)FBr$ and small amounts of peroxyxynitrate, $CF_2BrCFBrO_2NO_2$, and trifluorobromoethene epoxide.

$CF_2BrC(O)F$ was characterized by its IR spectrum consistent with both the proposed structure and the calculations carried out using *ab initio* and Density Functional Theory methods. In presence of CF_2CFBr the reaction proceeded with a pressure decrease. After the alkene was consumed an increase of the pressure and formation of bromine was observed. The oxidation is a chain reaction of pseudo-zero order with respect to O_2 as reactant at the pressure of oxygen used in this work. Its basic steps are: chain initiation by addition of NO_2 to the double bond leading, through reaction sequence in presence of O_2 , to generation of bromine atoms and chain propagation by reaction of Br^\bullet with alkene, originating $CF_2BrCFBrO_2^\bullet$ and $CF_2BrCFBrO^\bullet$ radicals. The predominant fate of the latter is the bromine atoms extrusion, with C-C bond cleavage playing only a minor role. A full mechanism is postulated. The value of $(2.2 \pm 1) \times 10^{-5} s^{-1}$ was obtained for the room temperature rate constant for the unimolecular decomposition of $CF_2BrCFBrO_2NO_2$.

Resumen

Se estudió la oxidación de CF_2CFBr por O_2 molecular iniciada por la adición de NO_2 al doble enlace del alqueno a 313,4 K en un sistema convencional estático. Se varió la presión inicial de CF_2CFBr entre 18,8 y 43,9 torr; la de NO_2 entre 0,9 y 4,8 torr y la de O_2 entre 96,9 y 402,9 torr. Se formaron los siguientes productos: $CF_2BrC(O)F$, como producto principal, $C(O)F_2$ y $C(O)FBr$ y pequeñas cantidades de peroxinitrato, $CF_2BrCFBrO_2NO_2$ y epóxido de trifluorobromoeteno. Se caracterizó el $CF_2BrC(O)F$ por su espectro infrarrojo comparándolo con el calculado usando métodos ab initio y la teoría de los funcionales de la densidad. En presencia de CF_2CFBr la reacción procede con disminución de la presión. Consumido el alqueno se observó aumento de la presión y la formación de bromo. A las presiones de oxígeno usadas en este trabajo, la oxidación es una reacción en cadena de pseudo-cero orden con respecto a O_2 como reactivo. Sus pasos básicos son: iniciación de cadena por adición de NO_2 al doble enlace, que en presencia de O_2 , mediante una secuencia de reacciones, genera los átomos de bromo y la propagación de la cadena por reacción de $Br\cdot$ con el alqueno, originando radicales $CF_2BrCFBrO_2\cdot$ y $CF_2BrCFBrO\cdot$. Este último se descompone principalmente por eliminación de átomo de bromo y en menor grado por la ruptura de enlace C-C. Se postuló el mecanismo completo de la reacción. Se obtuvo el valor de $(2,2\pm 1) \times 10^{-5} s^{-1}$ para la constante de descomposición unimolecular de $CF_2BrCFBrO_2NO_2$ a temperatura ambiente.

Introduction

In the reactions between NO_2 and halogenated olefins, NO_2 can act as nitrating or oxidating agent. The products of these reactions are nitrohaloacetyl halides and XNO , where $X = Cl$ or F , vicinal dinitro products and nitrohaloketones [1-8]. These works were generally executed for preparative purposes.

The detailed kinetic and mechanistic studies were reported for the thermal gas-phase reactions of NO_2 with CF_2CF_2 [9], CF_2CFCl , [10], CF_2CCl_2 [11], $CClHCCl_2$ [12], perfluoropropene, C_3F_6 , [13] and CF_2CFBr [14]. In these works a basic common reaction mechanism for nitration or oxidation of CX_2CX_2 by NO_2 , where $X = Cl, F$ or Br , can be postulated as follows:

1. $NO_2 + CX_2CX_2 \rightarrow CX_2(NO_2)CX_2\cdot$
2. $CX_2(NO_2)CX_2\cdot + NO_2 + M \rightarrow CX_2(NO_2)CX_2NO_2 + M$
3. $CX_2(NO_2)CX_2\cdot + NO_2 \rightarrow CX_2(NO_2)C(O)X + XNO$

The products of nitration of CF_2CF_2 were $CF_2(NO_2)C(O)F$ and FNO , those of CF_2CFCl were $CF_2(NO_2)CFCINO_2$, $CF_2(NO_2)C(O)F$ and $ClNO$ and those of CF_2CCl_2 were $CF_2(NO_2)CCl_2NO_2$, $CF_2(NO_2)C(O)Cl$ and $ClNO$. In the reaction of NO_2 with trichloroethene, NO_2 oxidizes $CClHCCl_2$, giving $HC(O)C(O)Cl$ and $ClNO$ as the only products [15]. The main products of the reaction between NO_2 and C_3F_6 were the oxidation product perfluoropropene oxide (PFPO) and nitric oxide, NO , produced in equivalent amounts. The dinitro- compound $CF_3CF(NO_2)CF_2NO_2$ and nitroperfluoroacetone $CF_3C(O)CF_2NO_2$ were also formed in minor amounts. The relation $R = \text{perfluoropropene oxide} / ([CF_3CF(NO_2)CF_2NO_2] + [CF_3C(O)CF_2NO_2])$ increased with temperature. In the reaction of NO_2 with CF_2CFBr the observed products were $CF_2(NO_2)C(O)F$, $CF_2(NO_2)CFBrNO_2$, $BrNO$, Br_2 and NO .

The addition of O₂ to the reaction system NO₂ + 1,1-dichlorodifluoroethene, changed the reaction course [16]. The oxidation of alkene, initiated by the addition of NO₂ to the double bond of the olefin, occurred, leading in presence of O₂ to the formation of nitroperoxy- radicals, CF₂(NO₂)CCl₂O₂• and nitrooxy- radicals, CF₂(NO₂)CCl₂O•. The CF₂(NO₂)CCl₂O• radicals released chlorine atoms, which add to 1,1-dichlorodifluoroethene originating radicals CF₂ClCCl₂O₂• and CF₂ClCCl₂O•. The free chlorine atoms generated from CF₂ClCCl₂O• radicals initiate a chain reaction with chlorine atoms as chain carriers, giving haloacetyl chloride, CF₂ClC(O)Cl as the main product. Some 15% of the CF₂ClCCl₂O• radicals decomposed by the scission of their C-C bond leading to the formation of C(O)F₂ and C(O)Cl₂ and reforming chlorine atoms. Also small amounts of peroxyxynitrate CF₂ClCCl₂O₂NO₂ and 1,1-dichlorodifluoroethene epoxide were formed.

The NO₂-initiated oxidation of tetramethylene was reported in literature [17]. The use of chemical initiators in absence of light permits a better control of the reaction course in organic synthesis. The stable and easily handled trifluoromethyl hypofluorite, CF₃OF, containing a weak O-F bond (43.5 kcal/mol) [18-20] is also an effective initiator of oxidation of haloalkenes (E). CF₃OF adds to the double bond giving CF₃O(E) radicals, where E = CF₂CCl₂ [21], CHClCCl₂ [22] and CCl₂CCl₂ [23]. The reaction of these radicals with O₂ is very fast leading to the formation of CF₃O(E)O, which principally decomposes by the detachment of the Cl from the CCl₂O group of the alkene. The chlorine atoms react rapidly with CX₂CCl₂, where X = H, Cl or F, initiating in presence of O₂, a chain reaction with Cl• as chain carrier and giving CX₂ClC(O)Cl as the main product. Minor amounts of C(O)X₂, where X = H, Cl and F, are also formed. In the case of C(O)HCl, it decomposes rapidly to CO and HCl.

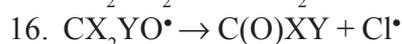
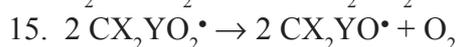
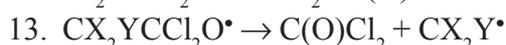
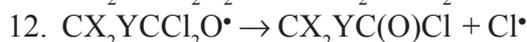
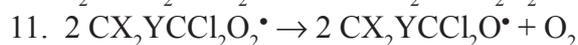
The direct Cl- and Br-atom initiated oxidation of CHClCCl₂ [24,25] and CCl₂CCl₂ [25] and Br-atom oxidation of CHClCCl₂ and CCl₂CCl₂ [26] were reported. These studies were made to investigate the atmospheric fate of trichloro- and tetrachloroethenes, used as solvents, dry cleaning agents and degreasing agents and released to the atmosphere in 90-100 % of their anthropogenic production.

The basic common chain reaction mechanism for the oxidation of haloalkenes, initiated by the addition of NO₂ or CF₃OF to the double bond of olefins in presence of O₂, and that initiated by ultraviolet or visible photolysis of Cl₂ and Br₂, can be resumed as:

Chain initiation by thermal reactions and photolysis

1. NO₂ + CX₂CCl₂ → R•
2. CF₃OF + CX₂CCl₂ → R• + F
3. F + CX₂CCl₂ → R•
4. R• + O₂ + M → RO₂• + M
5. 2 RO₂• → 2 RO• + O₂
6. RO• → R₁C(O)Cl + Cl• where R₁ = CX₂(NO₂), CX₂(CF₃O) or CX₂F
7. Br₂ $\xrightarrow{h\nu}$ 2 Br•
8. Cl₂ $\xrightarrow{h\nu}$ 2 Cl•

Chain Propagation by chlorine atoms as chain carriers



In this work the investigation of the reaction of NO_2 with bromotrifluoroethene, CF_2CFBr , in presence of molecular oxygen was undertaken to elucidate the elementary steps involved and to characterize the products. Comparing with the analogue reaction between NO_2 and chloroperfluoroalkene, CF_2CFCl in presence of oxygen [11], where free chlorine atoms are produced, it is reasonable to postulate that the free bromine atoms are formed in the reaction system $NO_2 + CF_2CFBr + O_2$. We have found no data on the addition of bromine atoms to fluorinated olefins.

Experimental

All reactants were purchased commercially. NO was eliminated from NO_2 (Matheson 99.5 %) by a series of freeze-pump-thaw cycles in presence of O_2 until disappearance of the blue colour of N_2O_3 . Finally, the degassed NO_2 was purified by fractional condensation using the fraction that distilled between 213 and 243 K. The CF_2CFBr (PCR, 97-98%) contained CF_4 , and CF_3CF_3 as impurities. These impurities are more volatile than CF_2CFBr , but could not be separated by fractional condensation, distilling together. The CF_2CFBr was purified by intermittent brief evacuation cycles at 153 K, opening and closing the trap valve. This procedure was repeated several times, until the disappearance of the respective very strong absorption bands of CF_4 [27] and CF_3CF_3 [28] at 1279 and 1250 cm^{-1} in the IR spectrum of CF_2CFBr . Oxygen was bubbled through 98 % analytical-grade H_2SO_4 and passed slowly through a Pyrex coil at 153 K.

The experiments were performed in a grease-free static system, allowing pressure measurements at constant volume and temperature. A spherical quartz bulb of 270 cm^3 ($S/V = 0.75 cm^{-1}$) was used as reaction vessel. The pressure was measured with a quartz spiral gauge and the temperature maintained within ± 0.1 K using a Lauda thermostat.

The reaction was followed measuring the pressure change as a function of time. 21 experiments were made at 313.4 K. The initial pressure of CF_2CFBr was varied between 18.8 and 43.9 torr, that of NO_2 between 0.9 and 4.8 torr and that O_2 between 96.9 and 402.9 torr. Initially the reaction proceeded with pressure decrease. After all CF_2CFBr was consumed a slow pressure increase was observed.

Infrared spectra of the reaction mixtures were recorded on a Shimadzu IR-435 spectrometer and a Perkin-Elmer 1600 Series FTIR spectrometer, using a 10 cm cell provided with NaCl and KBr windows, respectively. The gas FTIR spectra of the products, separated by fractional condensation after all alkene was consumed, were recorded on a Nexus Nicolet instrument

equipped with a cryogenic MCTB detector between 4000 and 400 cm^{-1} at room temperature, using a 10 cm cell provided with KBr windows. The UV-visible spectra of the products in the gas phase were recorded on a Hewlett-Packard Model 8452A spectrometer, using a 10 cm quartz cell.

Results

In the presence of CF_2CFBr the reaction proceeded with a pressure decrease, $-\Delta p/\Delta t$. After all the alkene was consumed the reaction continued with a slow pressure increase, $\Delta p/\Delta t$, as a function of time. No reaction between CF_2CFBr and O_2 was observed after several hours in the absence of NO_2 .

The following products were formed: $\text{CF}_2\text{BrC(O)F}$ as the main product, minor quantities of C(O)F_2 and C(O)FBr , and small amounts of $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$ and trifluorobromoethene epoxide (TFBrEO). The compound $\text{CF}_2\text{BrC(O)F}$ was characterized by its IR spectrum consistent with the *gauche* structure and with the calculations for this molecule using ab initio and Density Functional Theory methods [29]. The identification was confirmed by comparison with the experimental IR spectrum of $\text{CF}_2\text{ClC(O)F}$ [30], given that infrared spectra of analogous molecules, where the bromine atom is substituted by chlorine are similar. The most intense absorptions for this molecule are found to appear at 1887, 1195, 1102 and 937 cm^{-1} , and are assigned to the $\nu(\text{CO})$, $\nu_{as}(\text{CF}_2)$, $\nu_s(\text{CF}_2)$, and $\nu(\text{CF})$, respectively. The compounds C(O)F_2 [31] and C(O)FBr [32,33] were identified by their respective IR spectra and the formation of C(O)FBr was also detected by its UV spectrum at the range of 200-220 nm [33]. The product $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$ was identified by its infrared absorption band at 1758 cm^{-1} , characteristic to the NO_2 group of the haloalkylperoxynitrates and haloalkoxyperoxynitrate. This band appears at 1754 cm^{-1} for $\text{CCl}_3\text{O}_2\text{NO}_2$ [34-36], at 1757 cm^{-1} for $\text{CCl}_2\text{FO}_2\text{NO}_2$ [34-36], at 1761 cm^{-1} for $\text{CClF}_2\text{O}_2\text{NO}_2$ [34,35], at 1762 cm^{-1} for $\text{CF}_3\text{O}_2\text{NO}_2$ [37], at 1761 cm^{-1} for $\text{CF}_3\text{C(O)O}_2\text{NO}_2$ [38], at 1759 cm^{-1} for $\text{CClF}_2\text{C(O)O}_2\text{NO}_2$ [38], at 1755 cm^{-1} for $\text{CCl}_2\text{FC(O)O}_2\text{NO}_2$ [38], at 1755 cm^{-1} for $\text{CCl}_3\text{C(O)O}_2\text{NO}_2$ [38] and 1758 cm^{-1} for $\text{CF}_2\text{ClCCl}_2\text{O}_2\text{NO}_2$ [16]. The trifluorobromoethene epoxide (TFBrEO), was identified in the reaction mixture by its infrared band at 1540 cm^{-1} , assigned to the ring-breathing mode, characteristic of fluoroepoxides. This band appears at 1500 cm^{-1} for 1,1-dichloro-2,2-difluoroethene epoxide and chlorotrifluoroethene epoxide [39] and at 1551 cm^{-1} for perfluoropropene epoxide [13].

After the complete consumption of CF_2CFBr , the reaction continued with pressure increase, $\Delta p/\Delta t$, producing Br_2 and reforming NO_2 in addition to $\text{CF}_2\text{BrC(O)F}$, C(O)F_2 and C(O)FBr . The bromine was identified by its UV spectrum [40].

All experiments were carried out to the complete consumption of CF_2CFBr . For analyzing the reaction mixtures the reaction vessel was rapidly cooled to liquid air temperature and the mixture separated by fractional condensation. When the reaction was interrupted at the inflection point, when $-\Delta p/\Delta t$ changed to $\Delta p/\Delta t$, the first fraction Fr_1 , volatile at 158 K, consisted of C(O)F_2 and C(O)FBr , the second fraction Fr_2 , volatile at 183 K, was $\text{CF}_2\text{BrC(O)F}$ and the third fraction Fr_3 remaining as a residue at 158 K consisted of NO_2 and $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$. In the infrared spectrum of this fraction, weak absorption bands at 1321, 1025 and 821 cm^{-1} were observed. These bands are characteristic of the symmetric stretching of NO_2 in the C- NO_2 group and of the C-F and C-N groups, respectively, and were attributed to the presence of

traces of $\text{CF}_2\text{BrCFBrNO}_2$. The very strong band at 1618 cm^{-1} corresponding to the asymmetric stretching of NO_2 in the C-NO_2 group was overlapped by the broad band of NO_2 at $1635\text{--}1590\text{ cm}^{-1}$, suggesting that $\text{CF}_2\text{BrCFBrNO}_2$ was formed in very small amounts. When the reaction was interrupted while it proceeded with the pressure increase, the fractions Fr_1 and Fr_2 remained unchanged, but the fraction Fr_3 contained Br_2 in addition to $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$, NO_2 and $\text{CF}_2\text{BrCFBrNO}_2$.

The absence or presence of Br_2 in the reaction mixtures at different reaction time intervals corresponding to the pressure decrease and pressure increase, respectively, was monitored by UV spectroscopy.

It was observed in the successive infrared spectra of the same fraction Fr_2 , that intensity of the absorption band of $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$ at 1758 cm^{-1} decreases as a function of time, appearing bands of $\text{CF}_2\text{BrC(O)F}$ and very small bands of C(O)F_2 and C(O)FBr , and increasing the intensity of the band of NO_2 . In addition, the formation of Br_2 was detected by its UV spectra.

Considering that at low pressure the infrared absorption is proportional to the concentration of the corresponding compound, the value of $(2.2 \pm 1) \times 10^{-5}\text{ s}^{-1}$ was obtained for k , the effective room temperature rate constant for the unimolecular decomposition of $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$, measuring the absorbance A at 1758 cm^{-1} as a function of time t and using $k = \ln(A_m/A_n)/(t_m - t_n)$.

The reaction is a homogeneous chain reaction whose rate depends on the relation between NO_2 , CF_2CFBr and O_2 and the total pressure. At the pressures of O_2 used in this work, the reaction is of the pseudo-zero order with respect to O_2 as reactant, indicating the third body character of O_2 . The initial reaction rates were proportional to the respective pressures of NO_2 and CF_2CFBr and also were influenced in a specific way by the total pressure. At pressure of NO_2 and the temperature of our work, the equilibrium constant for $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$ [41] indicated that N_2O_4 was practically dissociated into NO_2 .

The behavior of the reaction rate, $-\Delta p/\Delta t$, as a function of time, corresponding to the pressure decrease interval, is illustrated in Figs. 1-3. The initial pressures of NO_2 , CF_2CFBr and O_2 in torr for each run presented are given inside the graphs. The analytical data of 10 experiments are summarized in the Table 1, where indices i and f signify initial and final, respectively.

Discussion

In order to propose the reaction mechanism, in addition to products analysis, the following reactions were considered: the reactions between NO_2 and CF_2CFCl [10], CF_2CCl_2 [11], CHClCCl_2 [12], and CF_2CFBr [14] in absence of O_2 , the reaction of NO_2 with CF_2CCl_2 in presence of O_2 [16], the oxidation of CF_2CCl_2 [21], CHClCCl_2 [22] and CCl_2CCl_2 [23] initiated by CF_3OF addition to the double bond, the bromine and chlorine atoms initiated oxidation of CHClCCl_2 [24,25] and CCl_2CCl_2 [25] and the respective oxidations of CHClCCl_2 and CCl_2CCl_2 [26] initiated by the bromine atoms.

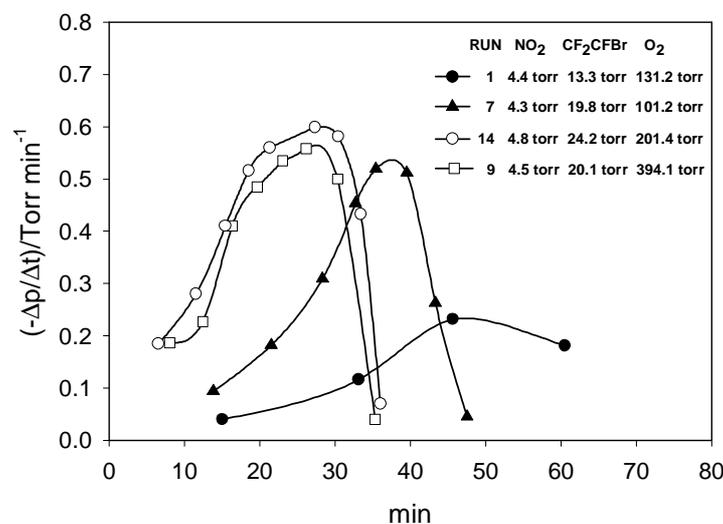


Fig. 1. Reaction rates, $-\Delta p/\Delta t$ as a function of time, corresponding to a pressure decrease interval. Initial pressures of NO_2 , CF_2CFBr and O_2 in torr for each run are given inside the graph.

The following mechanism appears to be consistent with the experimental results obtained in our work:

Chain initiation:

1. $\text{NO}_2 + \text{CF}_2\text{CFBr} \rightarrow \text{CF}_2(\text{NO}_2)\text{CFBr}^\bullet$
2. $\text{CF}_2(\text{NO}_2)\text{CFBr}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{CF}_2(\text{NO}_2)\text{CFBrO}_2^\bullet + \text{M}$
3. $2 \text{CF}_2(\text{NO}_2)\text{CFBrO}_2^\bullet \rightarrow 2 \text{CF}_2(\text{NO}_2)\text{CFBrO}^\bullet + \text{O}_2$
4. $\text{CF}_2(\text{NO}_2)\text{CFBrO}^\bullet \rightarrow \text{CF}_2(\text{NO}_2)\text{C}(\text{O})\text{F} + \text{Br}^\bullet$

Chain propagation:

5. $\text{Br}^\bullet + \text{CF}_2\text{CFBr} \rightarrow \text{CF}_2\text{BrCFBr}^\bullet$
6. $\text{CF}_2\text{BrCFBr}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{CF}_2\text{BrCFBrO}_2^\bullet + \text{M}$
7. $2 \text{CF}_2\text{BrCFBrO}_2^\bullet \rightarrow 2 \text{CF}_2\text{BrCFBrO}^\bullet + \text{O}_2$
8. $\text{CF}_2\text{BrCFBrO}_2^\bullet + \text{CF}_2\text{CFBr} \rightarrow \text{CF}_2\text{BrCFBrO}_2\text{CF}_2\text{CFBr}^\bullet$
9. $\text{CF}_2\text{BrCFBrO}_2\text{CF}_2\text{CFBr}^\bullet \rightarrow \text{CF}_2\text{BrCFBrO}^\bullet + \text{CF}_2\text{CFBr}$
10. $\text{CF}_2\text{BrCFBrO}^\bullet \rightarrow \text{CF}_2\text{BrC}(\text{O})\text{F} + \text{Br}^\bullet$
11. $\text{CF}_2\text{BrCFBrO}^\bullet \rightarrow \text{CF}_2\text{Br}^\bullet + \text{C}(\text{O})\text{FBr}$
12. $\text{CF}_2\text{Br}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{CF}_2\text{BrO}_2^\bullet + \text{M}$
13. $2 \text{CF}_2\text{BrO}_2^\bullet \rightarrow 2 \text{CF}_2\text{BrO}^\bullet + \text{O}_2$
14. $\text{CF}_2\text{BrO}^\bullet \rightarrow \text{C}(\text{O})\text{F}_2 + \text{Br}^\bullet$

Chain termination in presence of CF_2CFBr :

15. $\text{CF}_2\text{BrCFBrO}_2^\bullet + \text{NO}_2 + \text{M} \rightarrow \text{CF}_2\text{BrCFBrO}_2\text{NO}_2 + \text{M}$
16. $\text{CF}_2\text{BrCFBr}^\bullet + \text{NO}_2 \rightarrow \text{CF}_2\text{BrCFBrNO}_2$

Reactions after CF_2CFBr was consumed:

17. $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2 \rightarrow \text{CF}_2\text{BrC}\cdot\text{FBrO}_2 + \text{NO}_2$
7. $2 \text{CF}_2\text{BrCFBrO}_2\cdot \rightarrow 2 \text{CF}_2\text{BrCFBrO}\cdot + \text{O}_2$
8. $\text{CF}_2\text{BrCFBrO}\cdot \rightarrow \text{CF}_2\text{BrC}(\text{O})\text{F} + \text{Br}\cdot$
18. $\text{Br}\cdot + \text{NO}_2 \rightarrow \text{BrNO}_2$
19. $\text{Br}\cdot + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2$

Other steps were also considered: $\text{CF}_2(\text{NO}_2)\text{CFBr}\cdot + \text{NO}_2 + \text{M} \rightarrow \text{CF}_2(\text{NO}_2)\text{CFBrNO}_2 + \text{M}$ and $\text{CF}_2(\text{NO}_2)\text{CFBrO}_2\cdot + \text{NO}_2 + \text{M} \rightarrow \text{CF}_2(\text{NO}_2)\text{CFBrO}_2\text{NO}_2 + \text{M}$ but, as their products have not been detected, these reaction can be neglected in comparison with the steps of the chain reaction. Besides, they did not appear necessary to explain the results.

The primary path is the thermal addition of NO_2 to CF_2CFBr , giving $\text{CF}_2(\text{NO}_2)\text{CFBr}\cdot$ radicals. The corresponding rate constant for this reaction,

$k_1 = (1.51 \pm 0.45) \times 10^6 \exp(-10.88 \pm 1) \text{ kcal mol}^{-1}/\text{RT} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, was determined in a previous work [14]. The oxidation of $\text{CF}_2(\text{NO}_2)\text{CFBr}\cdot$ radicals leads through reactions (2) and (3) to the formation of $\text{CF}_2(\text{NO}_2)\text{CFBrO}\cdot$ radicals, which decompose giving bromine atoms. The bromine atoms initiate a chain reaction by their addition to the double bond of CF_2CFBr .

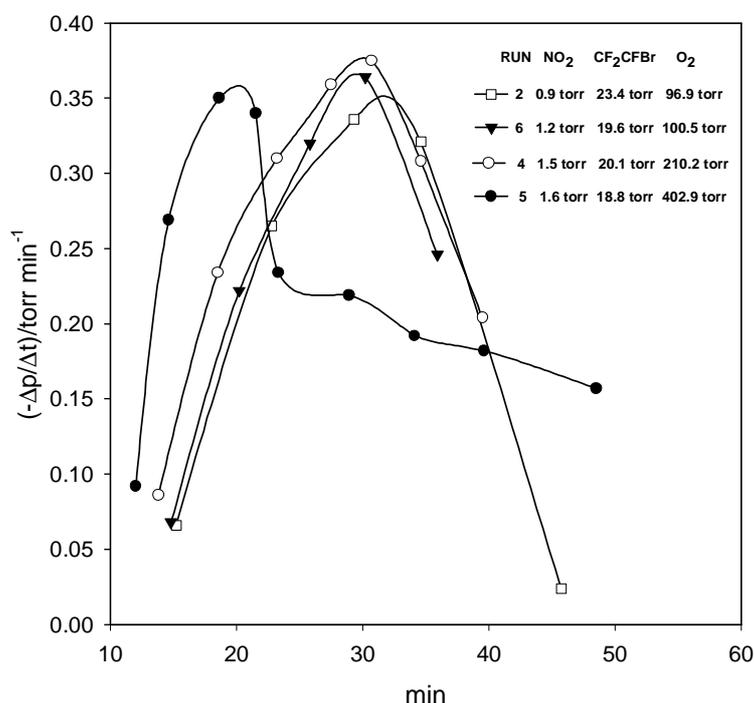


Fig. 2. Reaction rates, $-\Delta p/\Delta t$ as a function of time corresponding to a pressure decrease interval. Initial pressures of NO_2 , CF_2CFBr and O_2 in torr for each run are given inside the graph.

The formation of $\text{CF}_2\text{BrC}(\text{O})\text{F}$ as a principal product indicates that Br^\bullet atoms add to the CF_2 group of the alkene. We have found no published data on the reaction rate constants for the addition of bromine atoms to the double bond of fluorinated olefins. As in the presence of CF_2CFBr , bromine did not form, then the reaction (5) under the conditions of our work, must be more rapid, than the reaction (18) [42]. It indicates that the addition of Br^\bullet atoms to the fluorinated alkenes is faster than their reaction with chlorinated olefins. The reported room temperature rate constants for reactions of Br^\bullet with CHClCH_2 [43] and CH_2CCl_2 [43] are $(4.4 \pm 1.1) \times 10^8$ and $(2.2 \pm 0.4) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, those with CHClCCl_2 are $(6.6 \pm 2.4) \times 10^7$ [24,25], 9.4×10^7 [26] and $(5.4 \pm 1.1) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [43] and those with CCl_2CCl_2 are $(5.4 \pm 0.1) \times 10^4$ [25], $< 7 \times 10^4$ [26] and $< 6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [43]. The room temperature rate constant for the reaction of Br^\bullet with CH_2CH_2 is $7.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [26]. The addition of chlorine atoms to chloroethenes at 298 K is fast, of order of $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [44].

Only very small amounts of the termination product, $\text{CF}_2\text{BrCFBrNO}_2$, was formed through reaction (16), corroborating the almost complete elimination of $\text{CF}_2\text{BrCFBr}^\bullet$ radicals by O_2 . The equilibrium studies of $\text{CCl}_3^\bullet + \text{O}_2 \leftrightarrow \text{CCl}_3\text{O}_2^\bullet$ [45] and of $\text{R}^\bullet + \text{O}_2 \leftrightarrow \text{RO}_2^\bullet$ [46-48], where R^\bullet are alkyl radicals, suggest that the elimination of radicals $\text{CF}_2\text{BrCFBr}^\bullet$ should be almost complete at the oxygen pressure used in our work. It was reported by other authors, that the fraction of ethyl radicals that escape oxidation is $< 0.1\%$ at 2 torr of O_2 [49].

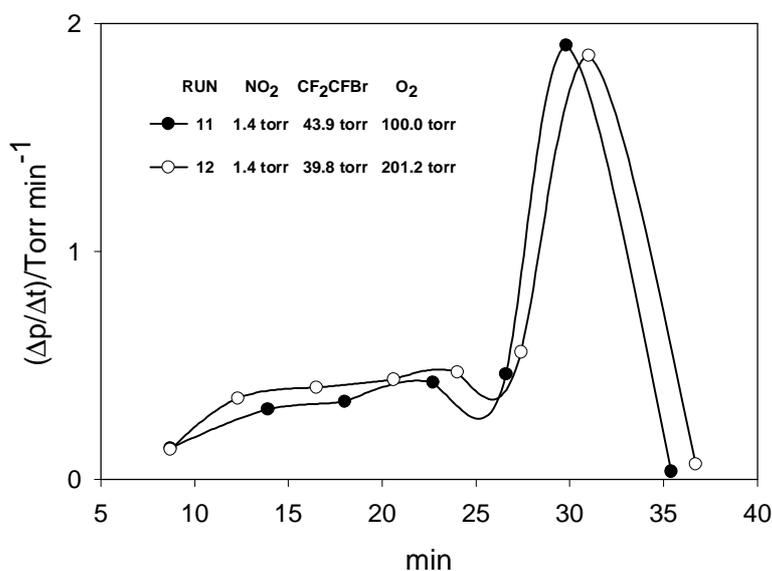


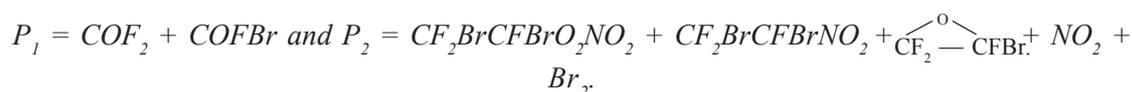
Fig. 3. Reaction rates, $-\Delta p/\Delta t$ as a function of time t , corresponding to a pressure decrease interval. Initial pressures of NO_2 , CF_2CFBr and O_2 in torr for each run are given inside the graph.

Under conditions of our work some peroxy radicals react with NO_2 to give $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$. The calculated rate constants for $\text{CX}_3\text{O}_2^\bullet + \text{NO}_2 \rightarrow \text{CX}_3\text{O}_2\text{NO}_2$, where $\text{X} = \text{H}, \text{F}, \text{Cl}$, are of order of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [36] and that reported for $\text{CF}_3\text{CFCIO}_2^\bullet + \text{NO}_2 + \text{M} \rightarrow \text{CF}_3\text{CFCIO}_2\text{NO}_2 + \text{M}$ is $(3.5 \pm 0.3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [50]. The formation of small amounts of trifluorobromoethene epoxide, indicates that a few radicals $\text{CF}_2\text{BrCFBrO}_2^\bullet$ add to the double

bond of alkene, reactions (8) and (9), regenerating $\text{CF}_2\text{BrCFBrO}^\bullet$. The epoxidation of alkenes by addition of peroxy radicals to the double bond, producing RO^\bullet radical and epoxide was reported [51]. The expression for k_a , the rate constant for the addition of peroxy radicals RO_2^\bullet to CF_2CCl_2 , obtained in our previous work [21], is $k_a = (1.9 \pm 1) \times 10^8 \exp(-4.8 \pm 1.4 \text{ kcal mol}^{-1} / \text{RT}) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The formation of $\text{CF}_2\text{BrC(O)F}$ as the major product, indicates that the main via of disappearance of peroxyradicals $\text{CF}_2\text{BrCFBrO}_2^\bullet$ is reaction (7) producing oxyradicals $\text{CF}_2\text{BrCFBrO}^\bullet$. The rate constant for the reaction $\text{RO}_2^\bullet + \text{RO}_2^\bullet \rightarrow 2 \text{RO}^\bullet + \text{O}_2$ are of order of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It was reported that rate constant for the self-reaction of $\text{CF}_3\text{CFCO}_2^\bullet$ to give $\text{CF}_3\text{CFCO}^\bullet$ is $(1.57 \pm 0.3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [50].

Table 1. Analytical data of 10 experiments carried out to the complete consumption of CF_2CFBr .



Run	T K	t min	CF_2CFBr torr	NO_{2i} torr	O_{2i} torr	O_{2f} torr	$\text{CF}_2\text{BrC(O)F}$ torr	P_1 torr	P_2 torr
2	313.4	190.0	23.4	0.9	96.9	83.0	19.8	8.0	1.1
3	313.4	125.8	21.2	1.5	198.3	186.0	17.4	6.8	1.5
5	313.4	105.0	18.8	1.6	402.9	391.5	15.6	6.4	1.8
6	313.4	94.0	19.6	1.2	100.5	88.7	16.0	6.4	1.5
7	313.4	181.7	19.8	4.3	101.2	88.7	15.6	6.2	4.0
14	313.4	36.5	24.2	4.8	201.4	186.2	19.2	7.6	4.4
8	313.4	35.0	21.7	4.4	234.2	220.7	17.2	6.8	4.2
9	313.4	46.6	20.1	4.5	394.1	381.1	15.9	6.4	4.1
10	313.4	48.1	43.9	1.4	100.0	74.1	36.4	14.6	1.8
11	313.4	36.3	39.8	1.4	201.2	177.7	33.4	13.4	1.5

The predominant fate of perhalogenated RO^\bullet is the halogen atom detachment, with C-C bond cleavage playing only a minor role. The elimination of Br^\bullet from the radical $\text{CF}_2\text{BrCFBrO}^\bullet$ can be explained in terms of concomitant weakening of the C-Br bond, when C-O bond is forming and the lower bond dissociation energy of the C-Br bond ($\sim 70 \text{ kcal/mol}$) as compared with the C-F bond ($\sim 110 \text{ kcal/mol}$). The extrusion of fluorine atom from perhalofluoromethoxy radicals is not expected as this process is highly endothermic [52]. The elimination of Br^\bullet from $\text{CF}_2\text{BrCFBrO}^\bullet$ predominates over C-C bond cleavage. The bond scission produces C(O)FBr and C(O)F_2 and bromine atoms through the reaction sequence (11)-(14).

The pre-exponential factors, A , and activation energies, E , obtained for the decomposition of radicals $\text{CF}_2\text{ClCCl}_2\text{O}^\bullet$ [21], $\text{CHCl}_2\text{CCl}_2\text{O}^\bullet$ [22] and $\text{CCl}_3\text{CCl}_2\text{O}^\bullet$ [23] were $A = (7 \pm 3) \times 10^{13} \text{ s}^{-1}$ and $E = 9.4 \pm 1.4 \text{ kcal mol}^{-1}$, $A = (1.1 \pm 1) \times 10^{14} \text{ s}^{-1}$ and $E = 9.4 \pm 2.4 \text{ kcal mol}^{-1}$, and $A = (3.0 \pm 1.4) \times 10^{13} \text{ s}^{-1}$ and $E = 9.7 \pm 1 \text{ kcal mol}^{-1}$, respectively. In the theoretical study of the

decomposition of halogenated alkoxy radicals [53] the following kinetic parameters were calculated for temperature range 240-260 K: $A = (4.06-4.49) \times 10^{13} \text{ s}^{-1}$ and $E = 9.7 \text{ kcal/mol}$ for $\text{CCl}_3\text{O}^\bullet$, $A = (2.85-3.1) \times 10^{13} \text{ s}^{-1}$ and $E = 10.6 \text{ kcal mol}^{-1}$ for $\text{CFCl}_2\text{O}^\bullet$, and $A = (2.85- 3.13) \times 10^{13} \text{ s}^{-1}$ and $E = 12.4 \text{ kcal mol}^{-1}$ for $\text{CF}_2\text{ClO}^\bullet$.

Molecular bromine is produced through reactions (17), (7), (8), (18) and the fast reaction (19), when all the alkene is consumed. Evidence was reported that the magnitude of the rate constant, k_{19} , falls between 10^9 and $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [42].

As the rate constant $k_{17} = (2.2 \pm 1) \times 10^{-5} \text{ s}^{-1}$ for the decomposition of $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$, is slow in comparison with those for the chain reaction steps, then in the time interval in which the alkene is present, the reaction (15) may be taken as a chain termination step together with the reaction (16). The reported room temperature rate constants for decomposition of $\text{CCl}_3\text{O}_2\text{NO}_2$ [54], $\text{CCl}_2\text{FO}_2\text{NO}_2$ [54], $\text{CClF}_2\text{O}_2\text{NO}_2$ [54], $\text{CF}_3\text{O}_2\text{NO}_2$ [55], $\text{CCl}_3\text{C(O)O}_2\text{NO}_2$ [54], $\text{CF}_3\text{O}_2\text{C(O)NO}_2$ [54], $\text{CF}_2\text{ClCCl}_2\text{O}_2\text{NO}_2$ [16] and $\text{CH}_3\text{C(O)O}_2\text{NO}_2$, PAN [56] are 0.19 , 6.6×10^{-2} , 4.0×10^{-2} , 6.1×10^{-2} , 1.2×10^{-4} , 8.0×10^{-5} , 1.3×10^{-4} and $3.2 \times 10^{-4} \text{ s}^{-1}$, respectively.

Applying the steady-state approximation to the mechanism in presence of alkene, the following expressions for the respective consumption of CF_2CFBr and NO_2 were obtained:

$$-d[\text{CF}_2\text{CFBr}]/dt = k_1[\text{NO}_2][\text{CF}_2\text{CFBr}] \{1 + (k_3/k_1)[\text{Br}^\bullet]/[\text{NO}_2] + (k_8/k_1)[\text{CF}_2\text{BrCFBrO}_2^\bullet]/[\text{NO}_2]\} \quad \text{I}$$

$$-d[\text{NO}_2]/dt = k_1[\text{NO}_2][\text{CF}_2\text{CFBr}] \{1 + (k_{15}/k_1) [\text{CF}_2\text{BrCFBrO}_2^\bullet] [\text{M}] / [\text{CF}_2\text{CFBr}] + (k_{16}/k_1)[\text{CF}_2\text{BrCFBr}^\bullet][\text{M}] / [\text{CF}_2\text{CFBr}]\} \quad \text{II}$$

Neglecting the contribution of the reactions of (4), (8) and (9) and assuming that $[\text{CF}_2\text{BrCFBr}^\bullet] \approx [\text{CF}_2\text{BrCFBrO}_2^\bullet]$, as practically all the radicals $\text{CF}_2\text{BrCFBr}^\bullet$ react with O_2 to give peroxyradicals $\text{CF}_2\text{BrCFBrO}_2^\bullet$, the following expression was deduced:

$$k_5 [\text{Br}^\bullet][[\text{CF}_2\text{CFBr}] = (k_{10} + k_{11}) [\text{CF}_2\text{BrCFBrO}^\bullet] = k_6 [\text{CF}_2\text{BrCFBr}^\bullet][\text{O}_2][\text{M}] \{1 - (k_{15}/k_6) [\text{NO}_2]/[\text{O}_2]\} \quad \text{III}$$

At the pressures of oxygen used in this work, O_2 has a third body character, as the reaction is of pseudo-zero order with respect to O_2 as reactant.

The chain velocity depends on the generation rate of the radicals $\text{CF}_2\text{BrCFBrO}^\bullet$ by reactions (5)-(7). Each oxy radical releases one bromine atom through reactions sequence (10)-(14), reforming the $\text{CF}_2\text{BrCFBr}^\bullet$ radicals. Decreasing the pressure of NO_2 , increases the generation of the chain carriers $\text{CF}_2\text{BrCFBrO}_2^\bullet$ and $\text{CF}_2\text{BrCFBrO}^\bullet$. With increasing generation of the radicals $\text{CF}_2\text{BrCFBrO}_2^\bullet$ the rate of the reaction (7) raises more rapidly that the rates of the reactions (8) and (15), favoring the formation of $\text{CF}_2\text{BrC(O)F}$ and the release of the bromine atom.

Conclusion

This investigation provides evidence, not reported until now, that the free bromine atoms can be released in the absence of light as a consequence of oxidation of CF_2CFBr initiated by addition of NO_2 to the double bond of trifluorobromoethene in the presence of molecular oxygen. The formation of bromodifluoroacetyl fluoride $\text{CF}_2\text{BrC(O)F}$ indicates that the bromine atoms add to the CF_2 group of the alkene, forming radicals $\text{CF}_2\text{BrCFBrO}_2^\bullet$ and $\text{CF}_2\text{BrCFBrO}^\bullet$ in the presence of oxygen. There are no data on the addition of Br^\bullet atoms to the fluorinated ethenes. The lack of formation of bromine in presence CF_2CFBr indicates that the addition of Br^\bullet atoms to the double bond competes successfully with the fast reactions $\text{Br}^\bullet + \text{NO}_2 \rightarrow \text{BrNO}_2$ and $\text{Br}^\bullet + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2$ and suggests that the reactions of bromine atoms with fluorinated alkenes are more rapid than those with the chlorinated counterpart. A new and simple way of preparation of $\text{CF}_2\text{BrC(O)F}$ is reported here. Previously it was prepared by catalytic reduction by lithium aluminum hydride of bromodifluoroacetate, obtained treating 1,2-dibromo-1-chlorotrifluoroethane with fuming H_2SO_4 and HgO [57]. The room temperature rate constant, $k_{17} = (2.2 \pm 1) \times 10^{-5} \text{ s}^{-1}$ for the decomposition of peroxyxynitrate, $\text{CF}_2\text{BrCFBrO}_2\text{NO}_2$ is presented for the first time.

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