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Formation of bromodifluoroacetyl fluoride, $CF_2BrC(O)F$, in the thermal gas-phase oxidation of bromotrifluoroethene, CF_2CFBr, initiated by trifluoromethylhypofluorite, CF_3OF

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Abstract

The oxidation of CF_2CFBr by molecular O_2, initiated by CF_3OF, has been studied at 273, 253.5, 239 and 218 K. The initial pressure of CF_3OF was varied between 0.9 and 2.4 Torr, that of CF_2CFBr between 11.5 and 30.7 Torr and that of O_2 between 42.5 and 100.7 Torr. The main product was $CF_2BrC(O)F$ (yields 81–95% based on the CF_2CFBr consumed). Minor amounts of $C(O)F_2$ and C(O)FBr and traces of bromotrifluoroethene epoxide were also formed. The reaction is a chain reaction with bromine atoms as chain carriers. Its basic steps are: the thermal generation of $CF_3O^\bullet$ radical by abstraction of fluorine atom from CF_3OF, chain initiation by addition of $CF_3O^\bullet$ to the double bond of alkene, leading, in presence of O_2, to the formation of bromine atom and chain propagation by the reaction of bromine atom with CF_2CFBr, originating $CF_2BrCFBrO^\bullet$ radical. The predominant fate of the latter is the bromine atom extrusion with C–C bond scission playing the minor role. The full mechanism is postulated.

Keywords: Thermal gas-phase oxidation; Bromotrifluoroethene; Trifluoromethylhypofluorite; Bromodifluoroacetyl fluoride

1. Introduction

The use of chemical initiators in absence of light permits better control of reaction course in organic synthesis. The stable and easily handled trifluoromethylhypofluorite, CF_3OF, containing a weak O–F bond (43.5 kcal/mol) [1,2,3] is an effective initiator of oxidation of haloalkenes and perfluoroolefins. The oxidations of CF_2CCl_2 [4], $CHClCCl_2$ [5] and CCl_2CCl_2 [6] in presence of CF_3OF are chain reactions with chlorine atoms as chain carriers, giving as the main products $CX_2ClC(O)Cl$, where X = H, Cl or F. Minor amounts of $C(O)X_2$, are also formed. In the case of C(O)HCl, it decomposes rapidly to CO and HCl. In the oxidation of CF_2CCl_2 [4] initiated by CF_3OF the formation of small quantities of 1,1-dichlorodifluoroethene epoxide was observed. The oxidations of perfluoropropene [7] and perfluorobutene-2 [8] initiated by CF_3OF are chain reactions with $CF_3O^\bullet$ radicals as chain carriers, giving $C(O)F_2$, $CF_3C(O)F$ and $CF_3OC(O)F$ as products. $CF_3OCF_2OCF_2C(O)F$ and a compound containing $CF(CF_3)OC(O)CF_3$ group are also formed in the respective oxidations of perfluoropropene and perfluorobutene-2.

Recently we have studied at 313.4 K the gas-phase oxidation of CF_2CFBr initiated by NO_2 [9], giving $CF_2BrC(O)F$ as the main product, minor equivalent amounts of $C(O)F_2$ and C(O)FBr, and small quantities of bromotrifluoroethene epoxide and peroxynitrate, $CF_2BrCFBrO_2NO_2$. It is a chain reaction propagated by bromine atoms. We have not found published data on the addition of bromine atoms to the fluorinated olefins. Only the Br-atom initiated oxidations of chlorinated ethenes with chlorine atoms as chain carriers, were reported [10–12].

In this work the oxidation of CF_2CFBr in presence of CF_3OF was studied.

2. Results and discussion

The experiments were carried out at 273, 253.5, 239 and 218 K. The initial pressure of CF_3OF was varied between 0.9 and 2.4 Torr, that of CF_2CFBr between 11.5 and 30.7 Torr and that of O_2 between 42.5 and 100.7 Torr.

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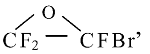
The products were identified by their infrared spectra after oxygen was eliminated from the reaction system. The main product was $CF_2BrC(O)F$ (yields 81–95% based on the CF_2CFBr consumed). Minor quantities of $C(O)F_2$ and C(O)FBr, traces of $CF_3OCF_2C(O)F$ and bromotrifluoroethene epoxide,  were also formed. The compound $CF_2BrC(O)F$ was characterized by its IR spectrum consistent with the *gauche* structure, by comparing it with the calculated one for this molecule using ab initio and Density Functional Theory methods [13]. For this molecule the most intense absorption bands appear at 1887, 1195, 1102 and 937 cm^{-1}, and are assigned to the $\nu(CO)$, $\nu_{as}(CF_2)$, $\nu_s(CF_2)$ and $\nu(CF)$, respectively. The compounds $C(O)F_2$ [14], C(O)FBr [15,16] and $CF_3OCF_2C(O)F$ [17] were identified by their respective IR spectra. The bromotrifluoroethene epoxide, present in the reaction mixture, was characterized by its infrared band at 1540 cm^{-1}, assigned to the ring-breathing mode, that is characteristic of fluoroepoxides. This band appears at 1500 cm^{-1} for 1,1-dichloro-2.2-difluoroethene epoxide [18], at 1545 cm^{-1} for chlorotrifluoroethene epoxide [18] and at 1551 cm^{-1} for perfluoropropene epoxide [19].

The very strong absorption band of CF_3OOCF_3 at 1166 cm^{-1} [20] and that of $CF_3C(O)F$ [21] at 1122–1119 cm^{-1} were not observed.

To determine the concentration of $CF_2BrC(O)F$ and that of non-consumed CF_2CFBr, the room temperature infrared calibration curves were made, using the pure compounds, thus allowing conversion of the absorption intensities at 1887 cm^{-1} to the pressures of $CF_2BrC(O)F$ and those at 1779 cm^{-1} to the pressures of CF_2CFBr. The pressures corresponding to the temperature of each run were calculated using the pressures of $CF_2BrC(O)F$ and CF_2CFBr at room temperature obtained from the calibration curves.

The analytical data of nine experiments are summarized in Table 1, where indices i and f denote initial and final and Δt is the time of permanence of the reaction system $CF_3OF + CF_2CFBr + O_2$ in the reaction vessel for each run. These data show that CF_2CFBr was completely consumed in the temperature range 273–239 K.

When the temperature of the reaction system, initially at 218 K, was raised rapidly to the room temperature without previously removing O_2, an explosion occurred with emission of light, giving CO_2, $C(O)F_2$, CF_4 and Br_2 as only products.

The reaction is a chain reaction. At the pressures of O_2 used in this work, the reaction does not depend on the concentration of O_2, showing the pseudo-zero order with respect to O_2 as reactant and indicating the third body character of O_2.

In order to propose the reaction mechanism, in addition to the analysis of the products, the following reactions were considered: the oxidations of CF_2CCl_2 [4], $CHClCCl_2$ [5] and CCl_2CCl_2 [6] initiated by addition of CF_3OF to the double bond and the oxidation of CF_2CFBr initiated by NO_2 [9].

The following reactions are consistent with the experimental results obtained in this work:

$$CF_3OF + CF_2CFBr \rightarrow CF_3CFBr^\bullet + CF_3O^\bullet \tag{1}$$

$$CF_3CFBr^\bullet + O_2 + M \rightarrow CF_3CFBrO_2^\bullet + M \tag{2}$$

$$2CF_3CFBrO_2^\bullet \rightarrow 2CF_3CFBrO^\bullet + O_2 \tag{3}$$

$$CF_3CFBrO^\bullet \rightarrow CF_3C(O)F + Br^\bullet \tag{4}$$

$$CF_3CFBrO^\bullet \rightarrow CF_3^\bullet + C(O)FBr \tag{5}$$

$$CF_3^\bullet + O_2 + M \rightarrow CF_3O_2^\bullet + M \tag{6}$$

$$2CF_3O_2^\bullet \rightarrow 2CF_3O^\bullet + O_2 \tag{7}$$

$$CF_3O^\bullet + CF_2CFBr \rightarrow CF_3OCF_2CFBr^\bullet \tag{8}$$

$$CF_3OCF_2CFBr^\bullet + O_2 + M \rightarrow CF_3OCF_2CFBrO_2^\bullet + M \tag{9}$$

$$2CF_3OCF_2CFBrO_2^\bullet \rightarrow 2CF_3OCF_2CFBrO^\bullet + O_2 \tag{10}$$

$$CF_3OCF_2CFBrO^\bullet \rightarrow CF_3OCF_2C(O)F + Br^\bullet \tag{11}$$

$$Br + CF_2CFBr \rightarrow CF_2BrCFBr^\bullet \tag{12}$$

$$CF_2BrCFBr^\bullet + O_2 + M \rightarrow CF_2BrCFBrO_2^\bullet + M \tag{13}$$

$$2CF_2BrCFBrO_2^\bullet \rightarrow 2CF_2BrCFBrO^\bullet + O_2 \tag{14}$$

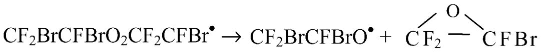
$$CF_2BrCFBrO_2^\bullet + CF_2CFBr \rightarrow CF_2BrCFBrO_2CF_2CFBr^\bullet \tag{15}$$

Table 1

Analytical data of nine experiments, where indices i and f denote initial and final and Δp is the time of permanence of reaction system $CF_3OF + CF_2CFBr + O_2$ in reaction vessel

Run	T (K)	Δt (min)	CF_3OF_i (Torr)	CF_2CFBr_i (Torr)	CF_2CFBr_f (Torr)	O_2 (Torr)	$CF_2BrC(O)F$ (Torr)
2	273.0	10.0	1.6	12.4	–	42.5	10.0
8	253.5	42.0	2.1	18.9	–	63.6	16.5
4	239.0	121.0	2.4	16.5	–	95.2	15.6
5	239.0	64.5	1.0	30.7	–	100.7	27.5
6	239.0	65.2	0.9	12.3	–	76.0	11.6
7	239.0	120.0	1.1	12.7	–	69.2	11.9
10	218.0	180.0	0.9	11.5	0.8	48.2	10.1
11[a]	218.0	180.0	0.9	20.7	–	65.9	–
13	218.0	66.5	1.0	19.0	13.5	66.3	5.2

[a] In this run the temperature of the reaction system $CF_3OF + CF_2CFBr + O_2$, initially at 218 K, was raised rapidly to room temperature without previously removing the oxygen. An explosion occurred with emission of light, giving CO_2, $C(O)F_2$, CF_4 and Br_2 as products.



$$CF_2BrCFBrO_2CF_2CFBr^\bullet \rightarrow CF_2BrCFBrO^\bullet + \overset{O}{CF_2 - CFBr} \quad (16)$$

$$CF_2BrCFBrO^\bullet \rightarrow CF_2BrC(O)F + Br^\bullet \quad (17)$$

$$CF_2BrCFBrO^\bullet \rightarrow CF_2Br^\bullet + C(O)FBr \quad (18)$$

$$CF_2Br^\bullet + O_2 + M \rightarrow CF_2BrO_2{}^\bullet + M \quad (19)$$

$$2CF_2BrO_2{}^\bullet \rightarrow 2CF_2BrO^\bullet + O_2 \quad (20)$$

$$CF_2BrO^\bullet \rightarrow C(O)F_2 + Br^\bullet \quad (21)$$

The primary path is the homolytic cleavage of a rather weak O–F bond in a bimolecular reaction between CF_3OF and CF_2CFBr, originating radicals $CF_3O^\bullet$. The radicals $CF_3O^\bullet$ add rapidly to the double bond forming $CF_3OCF_2CFBr^\bullet$ radical. The lack of formation of CF_3OOCF_3 confirms that the addition of $CF_3O^\bullet$ to the double bond is faster that any other reaction of this radical. The values of order 10^{10} $dm^3\,mol^{-1}\,s^{-1}$ were obtained for the addition of $CF_3O^\bullet$ to the alkenes [22–25].

The radicals $CF_3OCF_2CFBr^\bullet$ react with O_2, producing oxyradicals $CF_3OCF_2CFBrO^\bullet$ through the reactions (9) and (10). The equilibrium study of $R^\bullet + O_2 \leftrightarrow RO_2{}^\bullet$ [26], where $R^\bullet$ are alkyl radicals, suggests that at the pressure of O_2 used in this work the haloalkyl radicals generated in this reaction system are almost completely eliminated by O_2. It was also reported [27], that the rate constants for the reactions of methyl and halomethyl radicals with O_2 exceed those for fluorine-atom abstraction from CF_3OF by three to four orders of magnitude. It indicates that the reaction between radical $CF_3OCF_2CFBr^\bullet$ and CF_3OF to give the corresponding adduct $CF_3OCF_2CF_2Br$ and $CF_3O^\bullet$ can be neglected. The oxyradicals $CF_3OCF_2CFBrO^\bullet$ decompose eliminating bromine atoms, which, analogously to the chlorine atoms [4–6,28] add rapidly to the double bond, initiating the chain reaction and leading to the formation of radicals $CF_2BrCFBrO^\bullet$ in presence of O_2. The obtained products point out that the $CF_3O^\bullet$ and bromine atom add to the less bulky CF_2 group of the CF_2CFBr, which is consistent with the fact that the steric effects govern the addition process.

The formation of traces of bromotrifluoroethene epoxide, indicates that a few peroxy radicals $CF_2BrCFBrO_2{}^\bullet$ add to the double bond of CF_2CFBr, regenerating $CF_2BrCFBrO^\bullet$. The epoxidation of alkenes by addition of peroxy radical RO_2 to the double bond, producing $RO^\bullet$ radical and epoxide, was reported [29].

The production of $CF_2BrC(O)F$ as the main product indicates that at the temperature range 273–218 K the extrusion of $Br^\bullet$ from $CF_2BrCFBrO^\bullet$ predominates over the scission of the C–C bond.

No product of the reaction (4) was detected. It indicates that, in comparison to the chain reaction products, the amount of $CF_3C(O)F$ formed was not detectable.

3. Experimental

The experiments were performed in a grease-free conventional static system allowing pressure measurements at constant volume and temperature. A spherical quartz bulb with a volume of 270 cm^3 was used as reaction vessel. The pressure was measured with a quartz spiral gauge. Infrared spectra were recorded on a Shimadzu IR-435 spectrometer and a Perkin-Elmer 1600 Series FTIR spectrometer, using 10 cm cells provided with NaCl and KBr windows, respectively.

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 [30]. 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 [31] and CF_3CF_3 [32] at 1279 and 1250 cm^{-1} in the IR spectrum of CF_2CFBr. Oxygen (La Oxigena, 99.99%) was bubbled through 98% analytical-grade H_2SO_4, and passed slowly through a Pyrex coil at 153 K.

Fourteen experiments were made in the temperature range 273–218 K. The initial pressure of CF_3OF was varied between 0.9 and 2.4 Torr, that of CF_2CFBr between 11.5 and 30.7 Torr and that of O_2 between 42.5 and 100.7 Torr.

To eliminate the oxygen in excess from the reaction mixture, the reaction vessel was rapidly cooled down to liquid–air temperature and O_2 evacuated.

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