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Thermal gas-phase reaction of perfluorobuta-1,3-diene with NO_2

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Abstract

The reaction of NO_2 with perfluorobuta-1,3-diene, $CF_2{=}CFCF{=}CF_2$ (C_4F_6), has been studied at 312.9, 323.0, 333.4, 396.0 and 418.0 K, using a conventional static system. The products formed in the temperature range 312.9–333.4 K were $CF_2{=}CFCF(NO_2)CF_2(NO_2)$ (I), $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ (II), $CF_2{=}CFCF(NO_2)C(O)F$ (III) and $CF_2(NO_2)CF{=}CFC(O)F$ (IV) and FNO. The formation of these compounds was detected performing infrared and Raman spectra. The infrared spectrum shows a band at 1785 cm^{-1}, characteristic to the terminal $–CF{=}CF_2$ group and the Raman spectrum shows a band located at 1733 cm^{-1}, corresponding to $–CF{=}CF–$ group. It indicates, that in this temperature range, NO_2 attacks initially only one double bound of $CF_2{=}CFCF{=}CF_2$. Since the intermediate radical $CF_2{=}CFC^{\bullet}FCF_2(NO_2)$ formed in this process is allylic in nature, so there is no isomerization involved in this process, but rather the allylic radical is able to add the second NO_2 either to CF_2 or $CFCF_2(NO_2)$ end, forming the corresponding products. At 396.0 and 418.0 K different products were observed: $CF_2(NO_2)CF(NO_2)C(O)F$ (V), NO, $CF_3C(O)F$, $C(O)F_2$ and traces of epoxide of tetrafluoroethene, showing that, at these temperatures, both double bonds are attacked by NO_2 and detachment of CF_2 group is produced. The mechanisms consistent with experimental results in the temperature range 312.9–333.4 and at 396.0 and 418 K are proposed.

Keywords: Thermal gas-phase reaction; Perfluorobuta-1,3-diene; Nitrogen dioxide; 1,1,2,3,4,4–Hexafluoro-3,4-dinitrobut-1-ene; 2,3,4,4-Tetrafluoro-2-nitrobut-3-enoyl fluoride; 1,1,2,3,4,4-Hexafluoro-1,4-dinitrobut-2-ene; 2,3,4,4-Tetrafluoro-4-nitrobut-2-enoyl fluoride; 2,3,3-Trifluoro-2,3-dinitropropanoyl fluoride

1. Introduction

The addition reactions of NO_2 to halogenated olefins have been subject of several studies [1–9]. These reactions are generally employed for preparative purposes, because NO_2 can act either as nitrating or as oxidating agent. From a mechanistic point of view these processes are readily understood in terms of free radical reaction schemes initiated by the NO_2 attack on the olefinic C atom. As several reaction channels can be possible, the elucidation of the mechanism of these reactions is of interest for organic and inorganic chemistry.

Detailed mechanistic studies, kinetic parameters and product formation have been reported for several gas-phase reactions of NO_2 with perhalogenated ethenes CF_2CX_2, where X = Br, Cl or F, at temperatures ranging from about 300 to 360 K [10–12]. The major products in these systems were vicinal dinitro compounds and nitrohaloacetyl halides and XNO, where X = Br or Cl. The following basic common reaction mechanism can be proposed:

$$NO_2 + CF_2CX_2 \rightarrow CF_2(NO_2)CX_2^{\bullet}$$

$$CF_2(NO_2)CX_2^{\bullet} + NO_2 + M \rightarrow CF_2(NO_2)CX_2NO_2 + M$$

$$CF_2(NO_2)CX_2^{\bullet} + NO_2 \rightarrow CF_2(NO_2)C(O)X + XNO$$

In this mechanism and in the subsequent mechanisms of the present work M is equal to effective pressure.

However the gas-phase reactions of NO_2 with perfluoropropene, C_3F_6, [13] and with perfluorobutene-2, C_4F_8-2 [14] follow a different pattern.

Perfluoropropene reacts with NO_2 between 413.0 and 433.0 K [13], giving equivalent quantities of perfluoropropene epoxide, PFPE, and NO as the major products and smaller amounts of $CF_3CF(NO_2)CF_2(NO_2)$, nitroperfluoroacetone and FNO. The following mechanism was postulated for this

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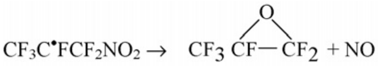
reaction:

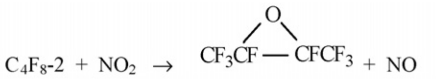
$$CF_3CF{=}CF_2 + NO_2 \rightarrow CF_3C^{\bullet}FCF_2NO_2$$

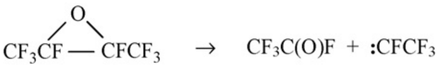


$$CF_3C^{\bullet}FCF_2NO_2 + NO_2 + M \rightarrow CF_3CF(NO_2)CF_2NO_2 + M$$

$$CF_3C^{\bullet}FCF_2NO_2 + NO_2 \rightarrow CF_3C(O)CF_2NO_2 + FNO$$

In the reaction of NO_2 with C_4F_8-2 in the temperature range 418.5–470.0 K [14], equal amounts of perfluorobutene-2 epoxide, PFBE, and NO are formed. Above 430 K PFBE decomposes generating $CF_3C(O)F$ and biradical **:**$CFCF_3$. The latter self-recombines reforming the parent C_4F_8-2 molecule. The following mechanism consistent with experimental results was postulated:





$$:CFCF_3 + :CFCF_3 + M \rightarrow C_4F_8\text{-}2 + M$$

Continuing our studies on nitration of perhalogenated olefins, the reaction of NO_2 with perfluorobuta-1,3-diene, C_4F_6, was investigated to elucidate the nitration mechanism of molecules containing two double bonds.

2. Results and discussion

All experiments were carried out to the complete consumption of NO_2. Within the temperature range 312.9–333.4 K the reaction proceeded with easily measurable pressure decrease and the following products were formed: $CF_2{=}CFCF(NO_2)CF_2(NO_2)$ (I), $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ (II), $CF_2{=}CFCF(NO_2)C(O)F$ (III) and $CF_2(NO_2)CF{=}CFC(O)F$ (IV) and FNO. The band at 1029 cm^{-1} appearing in the infrared spectra, assigned to SiF_4, confirms the presence of FNO. SiF_4 forms on Pyrex cell surface through the following reaction [9]:

$$SiO_2 + 4FNO \rightarrow SiF_4 + 2NO + 2NO_2.$$

At 396.0 and 418.0 K the NO_2 was completely consumed when introducing C_4F_6 to the reaction vessel as the second reactant. The observed products were $CF_2(NO_2)CF(NO_2)$-$C(O)F$ (V), NO, $CF_3C(O)F$, $C(O)F_2$ and traces of epoxide of tetrafluoroethene.

$CF_3C(O)F$, $C(O)F_2$, NO, FNO, SiF_4 and epoxide of tetrafluoroethene were identified by their known infrared spectra. The compounds (I), (II), (III) and (IV) have been assigned the structure consistent with their IR and Raman spectra. The infrared absorption bands for the mixture of $CF_2{=}CFCF(NO_2)CF_2(NO_2)$ (I) and $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ (II) appear at 1785, 1620, 1371, 1333, 1275, 1243, 1175, 1133, 925 and 790 cm^{-1}. In the infrared spectra of the mixture of $CF_2{=}CFCF(NO_2)C(O)F$ (III) and $CF_2(NO_2)CF{=}CFC(O)F$ (IV) the observed infrared bands were 1856, 1785, 1620, 1367, 1337, 1276, 1227, 1192, 1137, 931 and 813 cm^{-1}. In the Raman spectra of the mixture of compounds (I) and (II) and that of (III) and (IV), bands located at 1780 and 1733 cm^{-1} appeared. The infrared band at 1785 cm^{-1} is characteristic to the $–CF{=}CF_2$ group [15]. It was reported that 1783–1785 cm^{-1} band in the infrared spectrum of polytetrafluoroethene is indicative of the presence of terminal olefin groups in the structure of the polymer [16]. $CF_2{=}CFCF{=}CF_2$, $CF_3CF{=}CF_2$, $CClF{=}CF_2$ and $CBrF{=}CF_2$ show the bands corresponding to the C=C stretching vibrations at 1796, 1789, 1790 and 1783 cm^{-1}, respectively. It was reported [17] that the $–CF{=}CF–$ groups are not active in the infrared spectra. Indeed, the infrared spectrum of the perfluorobutene-2, $CF_3CF{=}CFCF_3$ shows a weak band corresponding to $–CF{=}CF–$ stretching vibration at 1728 cm^{-1}. At the same time the vibrations corresponding to internal double bond are usually active in the Raman spectra of perfluoroolefins and appear in the region 1717–1730 cm^{-1}. The vibrations corresponding to terminal olefin groups in the Raman spectra are located between 1775 and 1790 cm^{-1}. The bands at 1620 and 1333–1337 cm^{-1} are

Table 1
The comparison of experimental infrared and Raman spectra of A = $CF_2{=}CFCF(NO_2)CF_2(NO_2) + CF_2(NO_2)CF{=}CFCF_2(NO_2)$ and B = $CF_2{=}CFCF(NO_2)C(O)F + CF_2(NO_2)CF{=}CFC(O)F$

IR A	I_{IR}	Raman A	I_R	IR B	I_{IR}	Raman B	I_R	Tentative assigment
				1856	vs	1846	vvs	C=O
1785	s	1780	s	1785	s	1780	s	$–CF{=}CF_2$
		1733	s			1733	s	$–CF{=}CF–$
1620	vvs	1700	vvs	1620	vvs	1699	vvs	NO_2
1371	m	1412	s	1367	m	1412	s	C–C
1333	s	1341	vs	1337	s	1341	s	NO_2
1275	vs			1276	vs			CF_2
1243	vs			1227	vs			C–C
1175	m			1192	m			C–F
1133	m			1137	m			C–F
925	w			931	w			C–N
790	w			813	m			NO_2

I_{IR} = intensity in the infrared spectra, I_R = intensity in the Raman spectra, v = very, s = strong, m = medium and w = weak.

Table 2
Analytical data of three experiments in the temperature range 312.9–333.4 K, where P(I) = [$CF_2{=}CFCF(NO_2)CF_2(NO_2)$ + $CF_2(NO_2)CF{=}CFCF_2(NO_2)$] and P(II) = [$CF_2{=}CFCF(NO_2)C(O)F$ + $CF_2(NO_2)CF{=}CFC(O)F$]

Run	T (K)	Δp (Torr)	NO_{2i} (Torr)	NO_{2f} (Torr)	C_4F_{6i} (Torr)	C_4F_{6f} (Torr)	P(I) (Torr)	P(II) (Torr)	[FNO] (Torr)
9	312.9	25.5	33.5	–	34.5	17.9	8.7	8.0	7.9
8	323.0	23.0	30.1	–	30.8	15.7	8.0	7.0	6.9
7	333.4	26.8	32.9	–	28.3	12.0	10.4	6.0	6.1

The amounts of P(I) and P(II) were calculated from the quantities of C_4F_6 and NO_2 consumed, that of FNO formed and Δp, the final pressure decrease of the reaction.

characteristic to the NO_2 group [11–13,18]. The frequencies at 1367 and 1371 cm^{-1} and those between 1276 and 930 cm^{-1} indicate the presence of CF_2, CF, C–C and C–N groups. The absorption band located at 1856 cm^{-1} shows the presence of C(O)F group. It can be seen that the infrared and Raman spectra of the compounds (I), (II), (III) and (IV) are consistent with the structures proposed for $CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2(NO_2)CF{=}CFCF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$ and $CF_2(NO_2)CF{=}CFC(O)F$, respectively (see Table 1). The additional support for the characterization of the above compounds was obtained from the amounts of C_4F_6 and NO_2 consumed and that of FNO formed and the final pressure decrease of the reaction (see Table 2).

For the compound (V) the following structure has been assigned: $CF_2(NO_2)CF(NO_2)C(O)F$. Its infrared bands are located at 1856, 1617, 1333, 1275, 1242, 1192, 1133, 992 and 792 cm^{-1}. These frequencies indicate the presence of the structural groups: C(O)F, NO_2, CF_2, C–F, C–C and C–N. The determination of the relative molecular mass of this compound by gas-density measurement with a calibrated Pyrex bulb, gives the value 222 ± 11. The theoretical value of $CF_2(NO_2)CF(NO_2)C(O)F$ is 220.

In Table 1 the comparison of experimental infrared and Raman spectra of the mixtures: A = $CF_2{=}CFCF(NO_2)CF_2(NO_2)$ + $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ and B = $CF_2{=}CFCF(NO_2)C(O)F$ + $CF_2(NO_2)CF{=}CFC(O)F$ is presented.

No data for $CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$, $CF_2(NO_2)CF{=}CFC(O)F$ and $CF_2(NO)_2CF(NO_2)C(O)F$ were found in the literature. The formation of $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ in the reaction between N_2O_4 and C_4F_6 in the autoclave and at room temperature was reported [5].

No band in the region 1500–1550 cm^{-1} was observed, indicating that epoxide is not produced in this reaction. The fluorinated olefin epoxides generate a characteristic infrared band in this zone, not given by other fluorocarbon compounds. This band appears at 1551 cm^{-1} for perfluoropropene epoxide [13], at 1504 cm^{-1} for perfluorobutene-2 epoxide [14], at 1545 cm^{-1} for chlorotrifluoroethene epoxide and at 1500 cm^{-1} for 1,1-dichloro-2,2-difluoroethene epoxide [19].

For analyzing the reaction mixture of 8 experiments carried out to the complete consumption of NO_2, the reaction vessel was rapidly cooled to liquid nitrogen temperature and the mixture separated by fractional condensation. The fraction F_1, volatile at 153 K, obtained from experiments made in the temperature range 312.9–333.4 K was FNO and that from experiments performed at 396.0 and 418.0 K consisted of $CF_3C(O)F$, $C(O)F_2$, NO and epoxide of tetrafluoroethene. Over the whole temperature range 312.9–418.0 K studied, the fraction F_2, volatile at 233.0 K, was the non-consumed reactant C_4F_6. The fraction F_3, obtained as a residue at 233.0 K from experiments made in the temperature range 312.9–333.4 K, consisted of $CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2(NO_2)CF{=}CFCF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$ and $CF_2(NO_2)CF{=}CFC(O)F$, and that from experiments performed at 396.0 and 418.0 K was $CF_2(NO_2)CF(NO_2)C(O)F$.

$CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2(NO_2)CF{=}CFCF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$ and $CF_2(NO_2)CF{=}CFC(O)F$ cannot be separated by fractional condensation, but, distilling at 253 K, it was possible to obtain two fractions, one containing $CF_2{=}CFCF(NO_2)CF_2(NO_2)$ + $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ and another $CF_2{=}CFCF(NO_2)C(O)F$ + $CF_2(NO_2)CF{=}CFC(O)F$, with different relative amounts of these products thus allowing the assignment of the infrared frequencies corresponding to each mixture (see Table 1).

The analytical data of experiments in the temperature range 312.9–333.4 K are listed in Table 2, where indices i and f signify initial and final. The quantities of C_4F_6 consumed and that of FNO formed were obtained by fractional condensation. The amount of [$CF_2{=}CFCF(NO_2)CF_2(NO_2)$ + $CF_2(NO_2)CF{=}CFCF_2(NO_2)$] and that of [$CF_2{=}CFCF(NO_2)C(O)F$ + $CF_2(NO_2)CF{=}CFC(O)F$] were calculated from the quantities of C_4F_6 and NO_2 consumed, that of FNO formed and Δp, the final pressure decrease of the reaction.

The analytical data of experiments performed at 396.0 and 418.0 K are summarized in Table 3, where indices i and f

Table 3
Analytical data of 5 experiments at 396.0 and 418.0 K

Run	T (K)	NO_{2i} (Torr)	NO_{2f} (Torr)	$C_4F_6{}^r$ (Torr)	$CF_2(NO_2)CF(NO_2)C(O)F$ (Torr)	$\sum P$ (Torr)
5	396.0	33.7	–	25.1	11.2	16.8
3	418.0	19.0	–	40.9	6.5	9.3
4	418.0	27.6	–	33.7	9.8	13.8
10	418.0	33.5	–	21.4	11.1	16.0
11	418.0	47.7	–	51.2	16.4	24.6

In this table $C_4F_6{}^r$ is the pressure of C_4F_6 remaining after the total consumption of NO_2. $\sum P$ is the sum of the products [$CF_3C(O)F$] + [COF_2] + [NO] + [epoxide of CF_2CF_2].

denote initial and final. In this table $C_4F_6{}^{r}$ is the pressure of C_4F_6 remaining after the total consumption of NO_2. $\sum P$ is the sum of products [$CF_3C(O)F$] + [$C(O)F_2$] + [NO] + [epoxide of CF_2CF_2].

In the conditions of this work, the calculations done using the equilibrium constant for $N_2O_4 \leftrightarrow 2NO_2$ [20] indicate that N_2O_4 is practically dissociated into NO_2.

The reaction of C_4F_6 with NO_2 gives different products depending on the temperature region studied.

The following mechanism was postulated to explain the formation of $CF_2{=}CFCF(NO_2)CF_2NO_2$ (I) and $CF_2{=}CFCF(NO_2)C(O)F$ (III) in the temperature range 312.9–333.4 K:

$$CF_2{=}CFCF{=}CF_2 + NO_2 \rightarrow CF_2{=}CFC^{\bullet}FCF_2(NO_2)^{*} \tag{1}$$

$$CF_2{=}CFC^{\bullet}FCF_2(NO_2)^{*} + NO_2 + M \rightarrow CF_2{=}CFCF(NO_2)CF_2NO_2 + M \tag{2}$$

$$CF_2{=}CFC^{\bullet}FCF_2(NO_2)^{*} \rightarrow CF_2{=}CFC^{\bullet}FC(O)F + FNO \tag{3}$$

$$CF_2{=}CFC^{\bullet}FC(O)F + NO_2 \rightarrow CF_2{=}CFCF(NO_2)C(O)F \tag{4}$$

As NO_2 and C_4F_6 are stable compounds, the reaction must proceed by the addition of NO_2 to the double bond of the diolefin, analogously to other reactions of NO_2 with alkenes and dialkenes [10–14,21–23]. It was found that the initial attack by NO_2 occurs at the terminal position of the non-halogenated diolefins by C–N attachment giving $R'CH{=}CH^{\bullet}HCHR''(NO_2)$ radicals [21,24]. In presence of molecular oxygen peroxy radicals, $R'CH{=}CHC(O_2)^{\bullet}HCHR''(NO_2)$, are formed, which combine with NO_2 to yield peroxy nitrates, $R'CH{=}CHC(O_2NO_2)HCHR''(NO_2)$ [21]. In the present work the generation of the radical $CF_2{=}CFC^{\bullet}FCF_2(NO_2)$ was postulated, which may undergo reaction with another molecule of NO_2 giving $CF_2{=}CFCF(NO_2)CF_2NO_2$ or can decompose leading to the formation of FNO and $CF_2{=}CFC^{\bullet}FC(O)F$ radical. The latter radical reacts with the second NO_2 giving $CF_2{=}CFCF(NO_2)$-$CFCF(NO_2)C(O)F$.

Since the intermediate radical $(NO_2)CF_2C^{\bullet}FCF{=}CF_2$ formed by the addition of NO_2 to C_4F_6 is allylic in nature and there is no isomerization involved in this process, the allylic radical is able to add NO_2 either to $(NO_2)CF_2CF$ or CF_2 end. Then the formation of $CF_2(NO_2)CF{=}CFCF_2(NO_2)$ (II) and $CF_2(NO_2)CF{=}CFC(O)F$ (IV) can be explained by the reactions of the second NO_2 with the CF_2 end group:

$$(NO_2)CF_2C^{\bullet}FCF{=}CF_2{}^{*} + NO_2 + M \rightarrow CF_2(NO_2)CF{=}CFCF_2(NO_2) + M \tag{5}$$

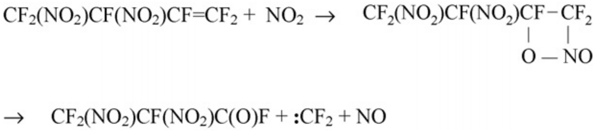
$$(NO_2)CF_2C^{\bullet}FCF{=}CF_2{}^{*} + NO_2 \rightarrow CF_2(NO_2)CF{=}CFC(O)F + FNO \tag{6}$$

The absorption band at 1785 cm^{-1} appearing in the infrared spectrum, indicative of the presence of $-CF{=}CF_2$ group and the band located at 1733 cm^{-1} in the Raman spectrum showing the presence of $-CF{=}CF-$ group, indicate that, in the temperature range 312.9–333.4 K, NO_2 does not attack the second double bond of C_4F_6 and the compounds $CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2(NO_2)CF{=}CFCF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$ and $CF_2(NO_2)CF{=}CFC(O)F$ are formed.

The following mechanism, where C_2F_4O is the epoxide of tetrafluoroethene, appears to be consistent with the experimental results obtained at 396.0 and 418.0 K:

$$NO_2 + CF_2{=}CFCF{=}CF_2 \rightarrow CF_2(NO_2)C^{\bullet}FCF{=}CF_2 \tag{1'}$$

$$NO_2 + CF_2(NO_2)C^{\bullet}FCF{=}CF_2 \rightarrow CF_2(NO_2)CF(NO_2)CF{=}CF_2 \tag{2'}$$



$$CF_2(NO_2)CF(NO_2)CF{=}CF_2 + NO_2 \rightarrow \begin{array}{c} CF_2(NO_2)CF(NO_2)CF-CF_2 \\ | \quad\;\; | \\ O-NO \end{array} \rightarrow CF_2(NO_2)CF(NO_2)C(O)F + {:}CF_2 + NO \tag{7}$$

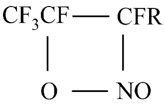
$$2\,{:}CF_2 \rightarrow CF_2{=}CF_2 \tag{8}$$

$$CF_2{=}CF_2 + NO_2 \rightarrow C_2F_4O + NO \tag{9}$$

$$C_2F_4O \rightarrow CF_3C(O)F \tag{10}$$

$$C_2F_4O \rightarrow C(O)F_2 + {:}CF_2 \tag{11}$$

The experimental results at 396.0 and 418.0 K are rationalized taking into account the data reported for the reactions $NO_2 + C_3F_6$ [13] and $NO_2 + C_4F_8$-2 [14], where the predominant process was the formation of NO and the corresponding epoxides of perfluoropropene and perfluorobutene-2. The formation of these products through the following four-member ring intermediate, where R=F or CF_3, was postulated:

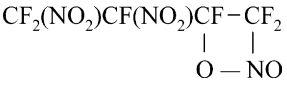


$$\begin{array}{cc} CF_3CF & -\!\!-\; CFR \\ | & | \\ O & -\!\!-\; NO \end{array}$$

The perfluoropropene epoxide and perfluorobutene-2 epoxide decompose above 460 and 430 K, respectively, the first giving $CF_3C(O)F$ and ${:}CF_2$ [25] and the latter $CF_3C(O)F$ and ${:}CFCF_3$ [14].

The lack of absorption band, characteristic to fluoro epoxides in the 1500–1550 cm^{-1} region of infrared spectra, shows that a stable compound containing epoxide group is not formed in this work.

Taking into account the above data, the concerted generation of $CF_2(NO_2)CF(NO_2)C(O)F$, ${:}CF_2$ and NO through a following four-center transition state is proposed:



$$\begin{array}{c} CF_2(NO_2)CF(NO_2)CF-CF_2 \\ | \quad\;\; | \\ O-NO \end{array}$$

It can be explained in terms of concomitant weakening and cleavage of C–C, C–N and O–NO bonds while C–O bond is forming.

The association of the two ${:}CF_2$ leads to the formation of $CF_2{=}CF_2$ and perfluorocyclopropane by addition of ${:}CF_2$ to tetrafluoroethene [25,26]. In presence of NO_2, perfluorocyclopropane does not form, but the generation of perfluoroethene epoxide is observed, indicating that the reaction of NO_2 with CF_2CF_2 leading to the formation of C_2F_4O, is faster than the addition of **:**CF_2 to the double bond. It is well known, that the perfluoroethene epoxide isomerizes to $CF_3C(O)F$ [27] and, at higher temperatures, decomposes unimolecularly to give $C(O)F_2$ and **:**CF_2 [28].

The nitric oxide NO did not add to the double bonds in this work. The fluoro compounds containing $–CF_2NO$ group have a characteristic intense blue color [29], which was not observed.

The reaction of C_4F_6 with FNO was discarded, because the addition of the latter compound to the double bond requires higher temperatures and pressures. No reaction between FNO and perfluorobutene-2 occurred below 473 K [30].

3. Conclusions

This work shows that below 335.0 K, NO_2 attacks only one double bond, giving three novel compounds: $CF_2{=}CFCF(NO_2)CF_2(NO_2)$, $CF_2{=}CFCF(NO_2)C(O)F$ and $CF_2(NO_2)CF{=}CFC(O)F$, and that above 390.0 K NO_2 reacts with the both double bonds, leading to the formation of another not reported compound $CF_2(NO_2)CF(NO_2)C(O)F$.

Density functional theory calculations to explore the reaction mechanism and characterize the molecular properties of these new molecules are underway [31].

4. Experimental

The experiments were performed in a conventional grease-free static system, allowing pressure measurements at constant volume and temperature. The spherical quartz bulb (270 cm^3), connected to a sensitive quartz spiral gauge, used as a null instrument, and to a mercury manometer, was employed as a reaction vessel. The reactor was also connected to a standard vacuum line for gas handling. The temperature was maintained within ±0.5 K using a Lauda thermostat, filled with Dow Corning 200/300 Fluid for temperatures above 360 K and with distilled water for those below 340 K. The infrared spectra were recorded on Shimadzu IR-435 spectrometer, using 10 cm cell provided with NaCl windows and the FTIR spectra on Nexus Nicolet instrument equipped with an MCTB, using 10 cm cell provided with Si windows with resolution of 1 cm^{-1} and 256 scans at different pressures. A Bruker IFS166 was used to record the FT Raman (6 mm tube, room temperature, excitation line 1064) spectra with 2 cm^{-1} resolution and 100 scans.

All reactants were purchased commercially. Perfluorobuta-1,3-diene, C_4F_6 (PCR, 97–98%) was purified by repeated low-pressure trap-to-trap distillation on vacuum line, the fraction distilling between 218 and 173 K being retained each time. Small amounts of NO present in NO_2 were eliminated by a series of freeze-pump-thaw cycles in presence of O_2 until the blue color due to the formation of N_2O_3 disappeared. The degassed NO_2 was purified by fractional condensation using fraction that distilled between 213 and 243 K.

The experiments were performed at 312.9, 323.0, 333.4, 396.0 and 418.0 K. In the temperature range of 312.9–333.4 K the initial pressure of NO_2 was varied between 30.1 and 33.5 Torr and that of C_4F_6 between 28.3 and 34.5 Torr. At 396 and 418.0 K the NO_2 was completely consumed when introducing C_4F_6 to the reaction vessel as the second reactant. In this case the initial pressure of NO_2 was varied between 19.0 and 47.7 Torr and the excess of non-consumed C_4F_6 varied between 21.4 and 51.2 Torr. The analysis of reaction mixtures was made by fractional condensation at 153 and 233 K. Three additional experiments were made at 418.0 K to obtain greater amounts of the compound $CF_2(NO_2)CF(NO_2)C(O)F$ (V) to determine its relative molecular mass. In these experiments the initial pressure of NO_2 varied between 71.3 and 202.9 Torr and the excess of non-consumed C_4F_6 varied between 78.5 and 234.0 Torr and only the fractional condensation at 233 K was performed.

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