

Radical addition of iodine monochloride to trifluoroethylene

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Abstract

The addition of iodine monochloride to trifluoroethylene (TrFE) leading to a ClCF₂CFHI (**I**)/ClCFHCF₂I (**II**) mixture is described. Four different ways of initiation (thermal, photochemical, presence of radical initiator, or redox catalyst) were used and all of them led to a high amount (>89%) of isomer (**I**). The amounts of (**I**) and (**II**) isomers were determined by ¹H and ¹⁹F NMR and also they were deduced from those of ClCF₂CFH₂ and ClCFHCF₂H obtained by selective reduction of the iodine atom of the former mixture, in the presence of tributylstannane. The reactivity of ICl to TrFE and the high proportion of isomer (**I**) were interpreted by means of a thermodynamical approach from the enthalpy of formation of (**I**) and (**II**), respectively, determined by semi-empirical computations. In addition, heats of formation of both isomers and interactions between SOMO of radicals and HOMO of fluoro-olefin enable to show that the mechanism of such a reaction occurs via the addition of I[•] to the less fluorinated side of TrFE. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Unlike vinylidene fluoride, chlorotrifluoroethylene and tetrafluoroethylene which have been extensively used in polymerization, telomerization [1] and radical additions, trifluoroethylene (TrFE) has been investigated in telomerization by few authors. The several telogens used may possess various bonds, cleaved by the initiation step in the process of telomerization: C–H [2], S–H [3,4], Si–H [5], C–I [6–12], C–Cl [13], C–Br [14–16], I–Cl [17].

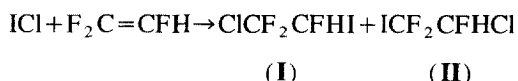
Table 1 lists the transfer agents, the ways of initiation and the amounts of normal and reversed adducts produced, since this alkene is unsymmetric.

Among these telogens, iodine monochloride has been used once with trifluoroethylene by photochemical initiation and in the presence of metals leading to the formation of both expected isomers ClCF₂CFHI (**I**) and ICF₂CFHCl (**II**) [17]. But, in the presence of AlCl₃, isomer CF₃CHClI and product CF₃CFHI were also produced beside (**I**) and (**II**) [17]. The goal of this paper concerns a deeper investigation of the addition of ICl to trifluoroethylene and involves a study of different ways of initiation in order to determine the best compromise between yield and selectivity (to isomer (**I**)). In addition, semi-empirical calculations give an understanding of the experimental observations.

2. Results and discussion

2.1. Addition of iodine monochloride to trifluoroethylene (TrFE)

In contrast to the hydrosilylation of trichlorosilane to TrFE [5], the radical addition of various transfer agents to this olefin led to a mixture of two isomers:



the 'normal' adduct (**I**) and the 'reverse' adduct (**II**), the ratio of which was determined by ¹⁹F and ¹H NMR spectroscopy.

The addition of ICl to such an alkene was performed with different ways of initiation and under various conditions (Table 2).

2.1.1. NMR characterization of isomers (**I**) and (**II**)

The ¹⁹F NMR spectrum exhibits two AB systems assigned to CF₂ groups of both isomers. The most abundant corresponds to ClCF₂CF_cHI and is represented by a doublet (²J_{F_aF_b} = 169.1 Hz) of doublets (³J_{F_aF_c} = 26.8 Hz) of doublets (³J_{F_aH} = 4.5 Hz) for F_a atom (δ = –62.4 ppm), and a doublet (²J_{F_bF_a} = 169.1 Hz) of doublets (³J_{F_bF_c} = 22.1 Hz) of doublets (³J_{F_bH} = 10.0 Hz) for F_b atom (δ = –64.9 ppm).

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Table 1
Telomerization of trifluoroethylene with different telogens (DBP and DTBP mean dibenzoyl peroxide and ditertiarybutyl peroxide, respectively)

Telogens	Initiation	Structures of Telomers	References
MeOH, Et ₂ O. MeCHO, THF	γ Rays	ROCHR'(C ₂ F ₃ H) _n H n=1-10	2
H ₂ S	X Rays	{ HCF ₂ CFHSH (85%) H ₂ CFCF ₂ SH (15%)	3
CF ₃ SH	hν	{ CF ₃ SCFHCFC ₂ H (98%) CF ₃ SCF ₂ CFH ₂ (2%)	4
Cl ₃ SiH	γ Rays	Cl ₃ SiCHFCF ₂ H (100%)	5
(CH ₃) ₃ SiH	γ Rays	{ (CH ₃) ₃ SiCF ₂ CH ₂ F (50%) (CH ₃) ₃ SiCFHCFC ₂ H (50%)	5
CF ₃ I, (CF ₃) ₂ CFI	hν	{ R _F CHFCF ₂ I (96%) R _F CF ₂ CFHI (4%)	6-9
	Thermal (190°C)	{ R _F CHFCF ₂ I (85%) R _F CF ₂ CFHI (15%)	6-10
CICF ₂ CFCIC ₂ F ₄ I	DBP (3h ; 110°C)	CICF ₂ CFCIC ₂ F ₄ (CFHCFC ₂) _n I n=1, 2, 3	11
Cl ₂ CFCFCII	DBP	Cl ₂ CFCFCI(C ₂ F ₃ H) _n I	12
CCl ₄	CuCl ₂ (80°C)	{ CCl ₃ CHFCF ₂ Cl CHFCICF ₂ CCl ₃	13
CF ₂ Br ₂	DBP	{ BrCF ₂ CF ₂ CFHBr (Min) BrCF ₂ CFHCFC ₂ Br (Maj)	14
CFBr ₃	hν	{ CFBr ₂ CFHCFC ₂ Br (Maj) CFBr ₂ CF ₂ CFHBr (Min)	15
CBr ₄ , CHBr ₃	DTBP	{ CBr ₃ CFHCFC ₂ Br (Maj) CBr ₃ CF ₂ CFHBr (Min)	16
ICI	UV or XCl ₃ (X=Fe or Al)	{ CICF ₂ CFHI (Maj) CICFHCFC ₂ I (Min)	17

Table 2
Addition of iodine monochloride to trifluoroethylene (TrFE): various reactions, conditions and methods of initiation (R_o , c_o and Ph_2CO mean $[\text{ICl}]_o/[\text{TrFE}]_o$, $[\text{initiator or catalyst}]_o/[\text{TrFE}]_o$ molar ratio and benzophenone; the yields were determined by gas chromatography; the experiments were performed in glass Carius tubes except for the thermal reactions carried out in Hastelloy autoclave)

Experiment no.	R_o	Initiator or catalyst	c_o	T (°C)	t (h)	Yield (%)	I/II (%)
1	1.04	sunlight	–	18	6	61	96/4
2	1.07	UV	–	19	6	65	96/4
3	1.05	$\text{Ph}_2\text{CO}/\text{sunlight}$	0.02	18	7	63	97/3
4	1.08	$\text{Ph}_2\text{CO}/\text{UV}$	0.02	19	7	66	97/3
5	1.11	CuCl	0.02	20	15	6	89/11
6	1.09	CuCl	0.02	140	6	34	98/2
7	1.08	AIBN	0.03	80	6	42	96/4
8	1.45	thermal	–	60	12	29	95/5
9	1.60	thermal	–	130	13	72	100/0

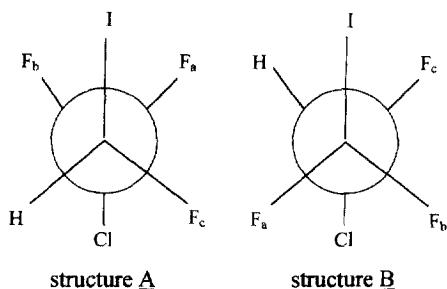


Fig. 1. Stable conformation of isomer I (structure A) and of isomer II (structure B).

The expected most stable conformer has the structure A (Fig. 1). The AB system with the smaller integration, assigned to isomer (II) ICF_2CFHCl , is a doublet ($^2J_{\text{FaFb}}=196.0$ Hz) of doublets ($^3J_{\text{FaFc}}=20.9$ Hz) of doublets ($^3J_{\text{FaH}}=3.0$ Hz) ascribed to F_a atom ($\delta=-54.7$ ppm), and a doublet ($^2J_{\text{FaFb}}=196.0$ Hz) of doublets ($^3J_{\text{FbFc}}=22.0$ Hz) of doublets ($^3J_{\text{FbH}}=6.8$ Hz) for F_b atom ($\delta=60.4$ ppm).

The most stable conformer of such a structure is B (Fig. 1).

It is interesting to note that the values of $^2J_{\text{FF}}$ coupling constant depend drastically on the environment of the difluoromethylene group and confirms $^2J_{\text{FF}}=164$ Hz for ClCF_2CFCI [18] and $^2J_{\text{FF}}=199.1$ Hz for ICF_2CFCI [19].

The X parts of the AB systems are high field shifted. That assigned to isomer (I) appears at -158.5 ppm as a doublet ($^2J_{\text{FcH}}=47.8$ Hz) of doublets ($^3J_{\text{FcFa}}=26.8$ Hz) of doublets ($^3J_{\text{FcFb}}=22.1$ Hz) whereas that with the smaller integration resonates at -142.5 ppm and represents a doublet ($^2J_{\text{FcH}}=48.4$ Hz) of doublets ($^3J_{\text{FcFa}}=20.8$ Hz) of doublets ($^3J_{\text{FcFb}}=21.9$ Hz).

The ^1H NMR spectrum exhibits two groups of signals. That centered at 6.9 ppm, assigned to isomer (I) represents a doublet ($^2J_{\text{HFc}}=47.8$ Hz) of doublets ($^3J_{\text{HFb}}=10.0$ Hz) of doublets ($^3J_{\text{HFa}}=4.5$ Hz) whereas the doublet ($^2J_{\text{HFc}}=48.5$

Hz) of doublets ($^3J_{\text{HFb}}=6.8$ Hz) of doublets ($^3J_{\text{HFa}}=3.0$ Hz) centered at 5.9 ppm is ascribed to isomer (II).

Table 2 lists the values of (I)/(II) ratio obtained from ^1H and ^{19}F -NMR of the products obtained from different initiating systems.

2.1.2. Influence of the initiation on the yield of the reaction and on the (I)/(II) ratio

Several ways of initiation have been chosen: photochemically, in the presence of cuprous catalyst or radical initiator, and finally thermally. In all these cases, the reactions were performed in batches and the conditions of the reaction were fixed by two initial molar ratios: R_o represents the molar ratio of $[\text{ICl}]_o$ to $[\text{TrFE}]_o$ whereas c_o is defined by the $[\text{catalyst or initiator}]_o$ to $[\text{fluoro monomer}]_o$ molar ratio. Usually, R_o was higher than 1 since our objective concerns the obtaining of the monoadduct. A ratio of 1.0 led to satisfactory results when chlorotrifluoroethylene was used as the fluorinated alkene [18]. c_o was about $1-4 \times 10^{-2}$ as used in previous work [1,18,20–22]. The reactions initiated photochemically or from metallic catalysts or radical initiators were performed in sealed Carius tubes, whereas those investigated thermally took place in Hastelloy autoclaves.

2.1.2.1. Photochemical initiation

As shown in Table 1, most telomerizations of trifluoroethylene have been initiated photochemically. Bissel [17] utilized this initiation which enabled the addition of ICl to such an olefin to lead to ClCF_2CFHI (I) and ICF_2CFHCl (II).

Our investigations were performed with two different UV sources: under sunlight and from a high pressure mercury lamp with or without benzophenone as photosensitizer (Table 2). Two different ways of stirring were utilized but did not influence the yield and the ratio of isomers: the Carius tube stood vertically, the reactants being stirred by means of a magnet bar or the tube was shaken mechanically describing a circle at a speed of 100 rpm. In these conditions, we have shown that the photochemical initiation yielded to two isomers (I) and (II) in 98/2 ratio.

Under similar conditions, the photochemical addition of ICl to trifluoroethylene is slower than to chlorotrifluoroethylene [18], since after 1.5 h-reaction complete conversion of ICl was not achieved in the first case, in contrast to the reaction involving CTFE. However, the former reaction appears as regioselective ((I)/(II)=98/2) as that using CTFE ($\text{ClCF}_2\text{CFCI}/\text{Cl}_2\text{CFCF}_2\text{I}=97/3$).

2.1.2.2. Redox catalysis

Redox catalysts are usually used in telomerization to favor the formation of low molecular weight-adducts and particularly the monoadduct [1,20–22]. Cuprous and cupric salts were utilized as catalysts and did not show great influence on the yield and on the ratio of isomers (Table 2). However, temperature has a drastic effect on them: the higher the temperature, the higher the yield and the lower the amount of

isomer (**II**). Interestingly, at 140°C the (**I**)/(**II**) ratio was 98/2 in contrast to 81/19 for isomers ClCF₂CFCII/Cl₂CFCF₂I produced by addition of ICl to CTFE [18].

2.1.2.3. Radical initiation

Various initiators were used for the addition of ICl to CTFE and AIBN was shown to be the most efficient [18]. Hence such an initiator was utilized (for 5 half lives to be sure that all the initiator generated radicals) for reacting ICl to trifluoroethylene. This reaction led to an (**I**)/(**II**) isomer ratio of 96/4 in 42% yield. Such a yield is slightly lower than that obtained for the radical addition of ICl to CTFE whereas the reaction seems more regioselective (normal/reverse isomer ratio was 92/8) when CTFE was used as the fluoro-olefin.

As noted for the radical addition of ICl to CTFE, no polytrifluoroethylene was produced. This can be explained by the assumed high transfer constant of ICl at 80°C, compared with perfluoroalkyl iodide which led to higher molecular weight telomers from the same R_o molar ratio [10].

2.1.2.4. Thermal initiation

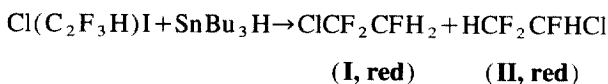
The thermal addition of ICl to trifluoroethylene was performed at 60°C and 130°C in a Hastelloy autoclave and was compared to the telomerization of this fluoro-olefin with perfluorobutyl iodide, C₄F₉CH₂CF₂I, (CF₃)₂CFI and C₅F₁₁CF(CF₃)I [10]. A previous study has shown that the more electrophilic the telogenic radical, the higher the amount of normal adduct and even at 190°C a telomeric distribution was produced from $R_o = 1$.

Interestingly, only the monoadduct was produced whatever the temperature and at 130°C, the reaction was regioselective leading to isomer (**I**), only. It can be assumed that Hastelloy metals may enhance the reaction, since at the same temperature similar reactions performed in a quartz Carius tube in the presence of cuprous chloride led to lower yields.

Indeed, whilst di- and triadducts have been observed for the telomerization of CTFE with ICl in the presence of a radical initiator [18], no propagation occurred when TrFE was used in the same conditions. This may be due to the reactive CFCII end-group [23] of I(CTFE)_xCl ($x = 1, 2$) telomers allowing them to be more efficient and thus leading to I(CTFE)_{x+1}Cl, as observed in the telomerization of CTFE with perfluoroalkyl iodides [24]. But, CFHI end-group of I(TrFE)Cl is less reactive than CFCII and thus does not enable higher molecular weight-telomers. However, in the case of TrFE, ICl appears as a very good transfer agent thanks to an easy cleavable bond, in contrast to perfluoroalkyl iodide [10] or methanol [2].

2.2. Reduction of (**I**)/(**II**) mixture

In order to confirm the structure of both (**I**) and (**II**) isomers, chemical substitution of the iodine atom was performed by tributylstannane as follows:



The reaction was selective on iodine and quantitative and has kept the same 97/3 isomer ratio. These derivatives were characterized as follows. Both ¹H and ¹⁹F NMR spectra of (**I, red**) were more simple than those of the precursor since the nuclei of ClCF₂ were not anisochronous. The chemical shift of the ClCF₂ group underwent a slight high field shift (centered at –62.6 ppm for (**I**) to –66.4 ppm for (**I, red**)) whereas that of the third fluorine atom was greater (from –158.5 ppm to –186.4 ppm for (**I, red**)). Similarly, the proton was high field shifted (from 6.90 ppm in (**I**) to 4.68 ppm).

The minor isomer exhibits a pseudo AB system (HCF₂) with a smaller $\Delta\delta$ and with a high field shift from ca. –57 (ICF₂) to –130 (HCF₂) whereas the CFHCl group underwent a slight low field shift from 5.90 ppm (isomer (**II**)) to 6.12 (isomer (**II, red**)).

2.3. Semi-empirical computations

We have attempted to explain the above results and to propose a reaction mechanism by means of quantum chemistry by using a thermodynamic approach and then an orbital approach. Since experimental values of heats of formation for our compounds are unavailable from the literature, we have used semi-empirical methods: MNDO [25] and AM1 [26] implemented in the MOPAC v.6.0 program [27]. Radicals, i.e., open shell systems, were treated by the Unrestricted Hartree–Fock (UHF) method, whereas the Restricted Hartree–Fock (RHF) method was used for closed shell systems. The precise option was employed to ensure very strict convergence criteria. The geometries of the reactants, products and radical intermediates were firstly fully optimized by Davidson–Fletcher–Powell (DFP) method [28,29]. In the same way, all stationary points were characterized as the true minima by the force method [30].

We have compared the reactivity of TrFE and CTFE with ICl according to a thermodynamic approach taking into account computations of heats of formation (ΔH_f) of different systems studied (reactants, intermediate radicals and products). Table 3 lists the results obtained from MNDO and AM1 methods. Interestingly, both these methods predict that isomers (**I**) ($\Delta H_f = -538.7$ kJ mol⁻¹ (AM1) and -537.0 kJ mol⁻¹ (MNDO)) and ClCF₂CFCII ($\Delta H_f = -513.4$ kJ mol⁻¹ (AM1) and -516.9 kJ mol⁻¹ (MNDO)) are more stable than isomers (**II**) ($\Delta H_f = -533.1$ kJ mol⁻¹ (AM1) and -525.4 kJ mol⁻¹ (MNDO)) and ICF₂CFCI₂ ($\Delta H_f = -510.8$ kJ mol⁻¹ (AM1) and -506.7 kJ mol⁻¹ (MNDO)), respectively. Such observations are in good agreement with experimental results since the most stable species are majority products but they deserve a deeper explanation. Actually, the use of a radical scavenger (e.g., 2,2-diphenyl-1-picryl-hydrazyl) in the case of the addition of ICl to CTFE [18] led to a decrease in yield. Hence, two radical mechanisms were suggested to produce ICFCICF₂Cl isomer in high amount: either that in which Cl[•] radical is added first to the less hindered side of the fluoro-alkene or a second

which surprisingly enables I[•] to react on the more hindered side of CTFE.

In order to explain such results, we have considered the radical reactivity which is often explained to terms of steric [31,32] and polar [31,32] effects, or by the thermodynamical [31–37] or orbital [34,35] controls.

From the experimental results (Ref. [18] and Table 2), an iodine atom prefers to be added on the less fluorinated sides of the fluoroolefins and thus on the more hindered part of CTFE: this disagrees with the influence of steric effects [31,32]. A similar behaviour has been observed by Tedder [31] showing that H₃C[•] reacts with the more hindered side of TrFE.

Considering thermodynamic control, we first calculated the heat of the different reactions which may occur. The heat of reaction (ΔH_r) can be related to the sum of the enthalpies of formation of the products (ΔH_{fp}) and of the reactants (ΔH_{fr}) as follows:

$$\Delta H_r = \sum(\Delta H_{fp}) - \sum(\Delta H_{fr})$$

The results are summarized in Table 4. It is observed that the addition of I[•] and Cl[•] to the less fluorinated site is always favoured thermodynamically even if the center is sometimes the more hindered. This confirms that both these reactions are not controlled by steric effects.

Actually, for the addition of I[•] to TrFE, Table 4 shows that the enthalpy of the reaction 5 (ΔH_{r5} is -31.6 kJ mol⁻¹ (AM1) and -33.0 kJ mol⁻¹ (MNDO)) (addition to the less fluorinated site) whereas $\Delta H_{r6} = 8.0$ kJ mol⁻¹ (AM1) and 6.0 kJ mol⁻¹ (MNDO) for the addition to the more halogenated site. On the other hand, the addition of I[•] to the less fluorinated carbon atom of CTFE leads to $\Delta H_{r7} = 15.0$ kJ mol⁻¹ (AM1) and -19.8 kJ mol⁻¹ (MNDO) whereas for that to the more fluorinated site, $\Delta H_{r8} = -4.3$ kJ mol⁻¹ (AM1) and -0.3 kJ mol⁻¹ (MNDO).

A similar behaviour is observed for the addition of Cl[•] to TrFE and to CTFE since the attack to the less fluorinated side of the alkene is the more exothermic (ΔH_{r9} and ΔH_{r11}). But, according to the experimental results, the chlorine atom is located mainly on the more fluorinated site. To us, iodine radical seems to react first and thus governs the observed experimentally regioselectivity.

These results can be confirmed by an orbital analysis by the means of the Frontier Molecular Orbitals Theory [38,39]. The results are gathered in Table 5 where SOMO, HOMO and LUMO represents the Single Occupied Molecular Orbital for the radical systems, the Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital of olefins, respectively. This table shows that interactions between SOMO of radicals and HOMO of the alkenes are the strongest, since the difference of energy between SOMO–LUMO is much greater than that of SOMO–HOMO.

Interestingly, SOMO of radical Cl[•] [$e_{\text{SOMO}}(\text{Cl}^\bullet) = -12.2$ eV (AM1) and -12.9 eV (MNDO)] is very deep compared with that of I[•] [$e_{\text{SOMO}}(\text{I}^\bullet) = -10.5$ eV (AM1) and -10.7 eV (MNDO)] and this latter is close to HOMO of both

Table 3

Calculated heats of formation (ΔH_f , kJ mol⁻¹) in the gas-phase at room-temperature of different systems studied

Products	AM1	MNDO	Exp. [42]	Literature [43]
I–Cl	-19.2	-28.0	17.8	
CHF=CF ₂	-545.7	-548.0	-489.9	-528.8
CCIF=CF ₂	-538.4	-547.2	-554.7	
IHFC–CF ₂ Cl	-538.7	-537.0		
IF ₂ C–CHFCl	-533.1	-525.4		
ICIFC–CF ₂ Cl	-513.4	-516.9		
IF ₂ C–CFCl ₂	-510.8	-506.7		
I [•]	106.7	106.7	106.7	
Cl [•]	121.2	121.2	121.2	
IHFC–CF ₂	-470.7	-474.3		
IF ₂ C–CHF	-431.1	-435.3		
CIHFC–CF ₂	-581.8	-594.2		
ClF ₂ C–CHF	-551.8	-568.0		
ICIFC–CF ₂	-446.7	-460.3		
IF ₂ C–CFCl	-436.0	-440.9		
Cl ₂ FC–CF ₂	-560.2	-574.1		
ClF ₂ C–CFCl	-555.3	-569.4		

Table 4

Calculated gas-phase enthalpies (ΔH_r , kJ mol⁻¹) for the proposed reactions

Reaction no.	Reaction	AM1	MNDO
1	I–Cl + CHF = CF ₂ → IHFC–CF ₂ Cl	26.3	39.0
2	I–Cl + CF ₂ = CHF → IF ₂ C–CHFCl	31.9	50.5
3	I–Cl + CCIF = CF ₂ → ICIFC–CF ₂ Cl	44.2	58.4
4	I–Cl + CF ₂ = CCIF → IF ₂ C–CFCl ₂	46.8	68.5
5	I [•] + CHF = CF ₂ → IHFC–CF ₂	-31.6	-33.0
6	I [•] + CF ₂ = CHF → IF ₂ C–CHF	8.0	6.0
7	I [•] + CCIF = CF ₂ → ICIFC–CF ₂	-15.0	-19.8
8	I [•] + CF ₂ = CCIF → IF ₂ C–CFCl	-4.3	-0.3
9	Cl [•] + CHF = CF ₂ → CIHFC–CF ₂	-157.2	-167.4
10	Cl [•] + CF ₂ = CHF → ClF ₂ C–CHF	-127.3	-141.2
11	Cl [•] + CCIF = CF ₂ → Cl ₂ FC–CF ₂	-143.0	-148.1
12	Cl [•] + CF ₂ = CCIF → ClF ₂ C–CFCl	-138.1	-143.4

Table 5

Frontier molecular orbital energies (eV) and atomic orbital coefficients of both sites of addition of olefin (C¹ and C²) in the HOMO and LUMO

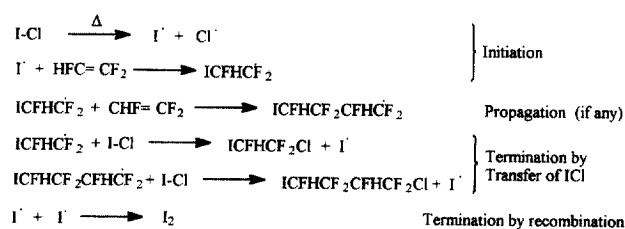
	SOMO		HOMO		LUMO	
	AM1	MNDO	AM1	MNDO	AM1	MNDO
I [•]	-10.50	-10.68				
Cl [•]	-12.19	-12.93				
C ¹ HF=C ² F ₂			-10.09	-10.46	-0.15	-0.62
2p _x (C ¹)			0.62	0.64	0.66	-0.67
2p _x (C ²)			0.54	0.58	-0.68	0.68
C ¹ ClF=C ² F ₂			-10.09	-10.69	-0.60	-1.17
2p _x (C ¹)			0.57	0.60	0.65	-0.65
2p _x (C ²)			0.53	0.56	-0.68	0.68

olefins [$e_{\text{SOMO}}(\text{olefin})$ is ca. -10 eV]. Consequently, Γ is added first to the alkene.

A more detailed explanation can be found by the orbital atomic coefficients of both ethylenic carbon atoms of Π orbital, according to the Frontier Molecular Orbital Theory [38,39] and from Canadell's rule [34,35]: a radical would be mainly added on the carbon atom having the greater coefficient in the HOMO.

As shown in Table 5, it is observed that the less fluorinated carbon atoms exhibit the greatest coefficients in Π orbitals: for TrFE ($2p_z(C^1) = \text{ca. } 0.62$, whereas $2p_z(C^2) = \text{ca. } 0.56$) and for CTFE ($2p_z(C^1) = \text{ca. } 0.58$, whereas $2p_z(C^2) = \text{ca. } 0.55$). Yet, it is noted that the difference between the coefficients of two carbon atoms of a given olefin in the HOMO is rather low. This can explain the absence of a total regioselectivity which depends upon experimental conditions (e.g., temperature, use of catalysts). However, if we consider the case of the addition of ICl to vinylidene fluoride ($\text{H}_2\text{C}^1=\text{C}^2\text{F}_2$) [40], only one isomer was produced and the different orbital atomic coefficients were the following: $2p_z(C^1) = 0.72$, whereas $2p_z(C^2) = 0.52$.

In conclusion, the addition of ICl to TrFE and CTFE undergoes a radical mechanism in which iodine radical reacts to fluoro-olefin first. Hence, the following mechanism can be proposed:



These first semi-empirical calculations are in good agreement with the experimental results. Indeed, they led to the conclusion that isomer (I) is the major product and is the most stable thermodynamically. This is evidence that the reactions were under thermodynamic control. The additions of Γ and Cl^\cdot radicals to both sites of unsymmetric CTFE and TrFE showed that the addition of Cl^\cdot was the most exothermic but it reacts to the less fluorinated site: this disagrees with experimental observation in contrast to the addition of Γ . However, on the basis of Frontier Molecular Orbitals, more explanations have been given.

In addition, the possibility of a concerted process may also be assumed and is under investigation [41].

3. Conclusion

Among four different initiation ways required for the radical addition of iodine monochloride to trifluoroethylene, the thermal way gives good yields and regioselective formation of ClCF_2CFHI isomer. This is the most convenient way since it does not require any expensive initiator or any metallic

catalysts regarded as toxic species. Interestingly, this thermal reaction was selective in monoaddition in contrast to that utilizing perfluoroalkyl iodides which produced telomeric distributions thus showing a high transfer constant of ICl. In addition no polytrifluoroethylene was observed.

Semi-empirical computations confirmed the formation of (I) as major isomer and indicated that the mechanism of such a reaction is mainly radical, Γ acting first on the CFH group of TrFE. However, deeper theoretical studies are required which are in progress.

Compared to chlorotrifluoroethylene, this fluoroalkene seems less reactive as far as the initiation method is concerned. Hence, comparison on reactivity, yield and regioselectivity of similar reactions involving hexafluoropropene, vinylidene fluoride and vinylidene chloride deserve to be studied and are under investigations.

4. Experimental

4.1. General comments

1,1,2-Trichloro-1,2,2-trifluoroethane was kindly supplied by Elf Atochem and Solvay. Iodine monochloride and tributylstannane were provided by Aldrich and did not require purification prior to use. Trifluoroethylene was supplied by Fluorochem.

After reaction, the whole product of the reaction or the products after work-up with alkali sodium bisulfite, were analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, $3 \text{ m} \times 1/8$ in (i.d). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260°C and 255°C , respectively. The temperature programme started from 50°C and reached 250°C at a heating rate of $15^\circ\text{C min}^{-1}$. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were characterized by ^1H and ^{19}F NMR spectroscopy at room temperature. The ^{19}F and ^1H NMR spectra were recorded on Bruker AC 200, 250 or WM 360 instruments, using deuterated chloroform and CFCl_3 as solvent and internal reference, for ^{19}F NMR and tetramethylsilane as reference for ^1H NMR. The letters d and t designate doublet and triplet, respectively. Coupling constants are given in hertz.

4.2. Radical addition of ICl to trifluoroethylene

When the initiation was performed photochemically or in the presence of AIBN or redox catalyst, the reactions were carried out in glass Carius tubes (2.5 mm thick, outside diameter: 20 mm and 175 mm long). After introduction of solid and liquid reactants under argon, trifluoroethylene was condensed in the Carius tube frozen in an acetone/liquid nitrogen

bath ($T = -80^\circ\text{C}$). The tube was sealed and then either irradiated with a UV source (mercury lamp Phillips HPK 125 W) at room temperature or under sunlight (experiments 1–4 in Table 2), or placed in the cavity of a thermoregulated oven and heated while shaking (experiments 5–7). At the end of the reaction, the tubes were cooled with liquid nitrogen and opened.

For example in experiment 4, trifluoroethylene (3.8 g, 46.3 mmol) was condensed into a Carius tube containing ICl (8.1 g, 50.0 mmol), benzophenone (0.169 g, 0.9 mmol) and 10 g of methylene chloride. Chlorobenzene was used as the external standard. The yield was calculated from the calibration curve $A(\text{ClC}_2\text{F}_3\text{HI})/A(\text{standard})$ vs. $\text{weight}(\text{ClC}_2\text{F}_3\text{HI})/\text{weight}(\text{standard})$ determined by GC (A designated the area of the peak assigned to the product).

The reactions performed under thermal initiation (experiments 8 and 9) were carried out in a HC 276 200-ml Hastelloy autoclave. First, the vessel was charged with the required amounts of ICl and methylene chloride and closed. It was then cooled in an acetone/liquid nitrogen mixture to condense trifluoroethylene, after two cycles of degassing with nitrogen under pressure followed by vacuum. By double weighing, a suitable amount of gas was introduced under pressure and trapped. The autoclave was then brought to the desired temperature and the reaction medium was stirred during the reaction with a magnet bar. After the reaction, the vessel was cooled down to room temperature, then put into ice while the non-reacted TrFE was released.

For example in experiment 9, trifluoroethylene (18 g, 0.22 mol), ICl (57.1 g, 0.35 mol), and 50 g of methylene chloride were stirred at 130°C for 13 h. After reaction, 4.3 g (mainly unreacted TrFE) were released and after opening the autoclave, the whole was distilled. After removal methylene chloride, the monoadduct was rectified, $\text{Bp} = 47^\circ\text{C}$, 38.6 g, 0.16 mol of a colourless liquid were obtained (yield = 72%).

Isomers (I) and (II) have not been separated from each other.

Isomer (I): 1-chloro-1,1,2-trifluoro-2-iodo ethane $\text{ClCF}_a\text{F}_b\text{CF}_c\text{HI}$ ^{19}F NMR (CDCl_3) δ : AB system at -62.4 (ddd, $^2J_{\text{FaFb}} = 169.1$, $^3J_{\text{FaFc}} = 26.8$ and $^3J_{\text{FaH}} = 4.6$, Fa), and -64.9 (ddd, $^2J_{\text{FaFb}} = 169.1$, $^3J_{\text{FbFc}} = 22.1$ and $^3J_{\text{FbH}} = 10.0$, Fb); X part of ABX system: -158.5 (ddd, $^2J_{\text{HFc}} = 47.8$, $^3J_{\text{FcFa}} = 26.8$, $^3J_{\text{FcFb}} = 22.1$, Fc).

^1H NMR (CDCl_3) δ : 6.9 (ddd, $^2J_{\text{HFc}} = 47.8$, $^3J_{\text{HFb}} = 10.0$, $^3J_{\text{HFa}} = 4.6$).

Isomer (II): 1-iodo-1,1,2-trifluoro-2-chloro-ethane $\text{ICF}_a\text{F}_b\text{CF}_c\text{HCl}$.

^{19}F NMR (CDCl_3) δ : AB system at -54.7 (ddd, $^2J_{\text{FaFb}} = 196.0$, $^3J_{\text{FaFc}} = 20.9$, $^3J_{\text{FaH}} = 3.0$, Fa) and at -60.4 (ddd, $^2J_{\text{FaFb}} = 196.0$, $^3J_{\text{FbFc}} = 22.0$, $^3J_{\text{FbH}} = 6.8$, Fb); X part of ABX system: -142.5 (ddd, $^2J_{\text{FCH}} = 48.5$; $^3J_{\text{FcFa}} = 20.9$; $^3J_{\text{FcFb}} = 22.0$).

^1H NMR (CDCl_3) δ : 5.90 (ddd, $^2J_{\text{HFc}} = 48.5$, $^3J_{\text{HFb}} = 6.8$, $^3J_{\text{HFa}} = 3.0$).

4.3. Reduction of (I)/(II) mixture into (I, red)/(II, red)

In a two necked round bottom flask equipped with a Vigreux column fitted with a condenser was introduced under argon 5.0 g (0.02 mol) of $\text{IC}_2\text{F}_3\text{HCl}$. 6.0 g (0.02 mol) of tributylstannane was added dropwise at room temperature through a septum.

(I, red)/(II, red) mixture was trapped in a round bottom flask containing 1,1,2-trifluoro-1,2,2-trichloroethane (F-113) cooled in a NaCl/ice bath during its distillation as soon as formed.

Isomer (I, red): 1-chloro-1,1,2-trifluoroethane $\text{H}_2\text{CFCF}_2\text{-Cl}$.

^{19}F NMR (CDCl_3 and F113) δ : -66.4 (dt, $^3J_{\text{FF}} = 21.1$, $^3J_{\text{FH}} = 10.4$, 2F); -186.4 (tt, $^2J_{\text{FH}} = 46.2$; $^3J_{\text{FF}} = 21.1$, 1F).

^1H NMR (CDCl_3 and F-113) δ : 4.68 (dt, $^2J_{\text{HF}} = 46.2$, $^3J_{\text{HF}} = 10.4$).

(II, red): 1,1,2-trifluoro-2-chloroethane $\text{HCF}_a\text{F}_b\text{CF}_c\text{HCl}$.

^{19}F NMR (CDCl_3 and F-113) δ : pseudo AB system -129.4 (dddd, $^2J_{\text{FaFb}} = 231.0$, $^2J_{\text{FaH}} = 54.2$, $^3J_{\text{FaFc}} = 21.0$, $^3J_{\text{FaH}} = 5.6$, Fa); -130.9 (dddd, $^2J_{\text{FbFa}} = 231.0$, $^2J_{\text{FbH}} = 54.2$, $^3J_{\text{FbFc}} = 20.8$, $^3J_{\text{FbH}} = 5.6$, Fb); -158.6 (dddd, $^2J_{\text{FCH}} = 49.1$, $^3J_{\text{FcFa}} = 21.0$, $^3J_{\text{FcFb}} = 20.8$, $^3J_{\text{FCH}} = 3.6$, Fc).

^1H NMR (CDCl_3 and F-113) δ : 5.85 (tdd, $^2J_{\text{HF}} = 54.2$, $^3J_{\text{HFc}} = 3.6$, $^3J_{\text{HH}} = 3.5$, HCF_2); 6.12 (dtd, $^2J_{\text{HFc}} = 49.1$, $^3J_{\text{HF}} = 5.6$, $^3J_{\text{HH}} = 3.9$, CFHCl).

5. Supporting materials

MOPAC output files of all optimized molecules may be obtained from the authors.

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