

ELECTROCHEMICAL REDUCTION OF CF_2Br_2 IN THE PRESENCE OF RICH OR DEFICIENT OLEFINS

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Abstract: In the presence of an olefin, CF_2Br radicals add to the double bond with a constant rate that depends only modestly on the olefin nature (1-hexene, 2.3-dimethyl-2-butene and ethylacrylate). However, the fate of the radical adduct depends on the nature of the olefin and controls the nature of the main electrolysis product(s). For 1-hexene, the radical adduct abstract a Br-atom from the parent CF_2Br_2 . This triggers a rapid radical chain reaction, which results overall in the addition of CF_2Br_2 across the double bond. For ethylacrylate, the radical adduct adds to the parent olefin, which initiate oligomerisation. For 2.3-dimethyl-2-butene, the radical adduct undergoes dismutation. Cyclopropanation is observed only with 2.3-dimethyl-2-butene and corresponds to a fast trapping of the carbene CF_2 before it may react with DMF. For the two other olefins, reaction of CF_2 with DMF is preferred.

Keywords: *reduction, olefin, radical adduct, number of electrons, preparative electrolysis*

When the same voltammetric experiments [1] as in Figure 1 are repeated in the presence of increasing amounts of olefins, the general features of the voltammograms are conserved yet one observes a significant decrease of the CF_2Br_2 reduction peak height, together with a reduction of the oxidation wave for bromide ions observed upon scan reversal. It is noteworthy that while the decrease of the CF_2Br_2 reduction peak is independent of the scan rate and does not appear to be very dependent on the nature of the olefin, it is larger the concentration of olefin (compare with Figure 2).

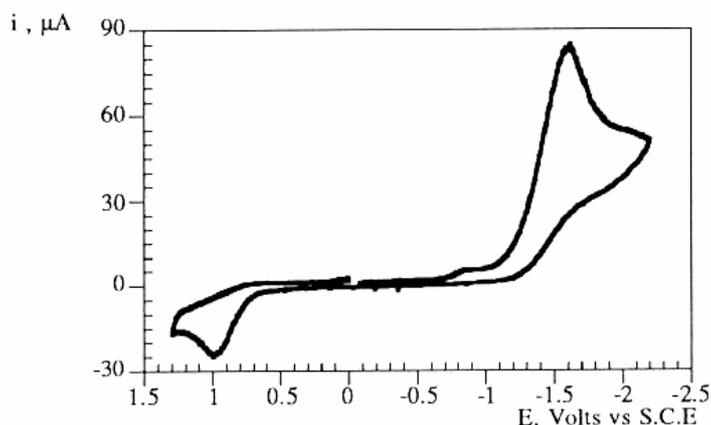


Figure 1: LSV of CF_2Br_2 : $\nu = 100 \text{ mV} \cdot \text{s}^{-1}$, $C_0 = 3,3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Glassy carbon disk 3 mm in diameter. DMF -TBAF 0.05 M (tetrabutylammoniumtetrafluoroborate). Potential referenced to calomel electrode saturated in KCl (SCE). Auxiliary electrode: platinum wire. The peak is situated at -1.68 Volt /SCE. Program of potential: 0, -2.2, +1.3, 0 Volt /SCE. Measurements under nitrogen. The small wave at -0.9 V is corresponding to residual oxygen.

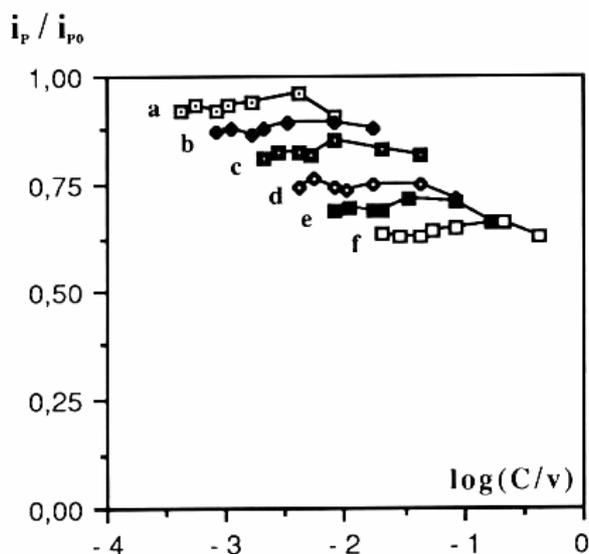


Figure 2a: Case of 2,3-dimethyl-2-butene $i_p/i_{p0} = f(\log(C/\nu))$. C: concentration of 2,3-dimethyl-2-butene: a,b,c,d,e,f respectively correspond to 0.84, 1.68, 4.2, 8.41, 16.8 and 42 mM, ν speed of variation of potential (V/sec.)

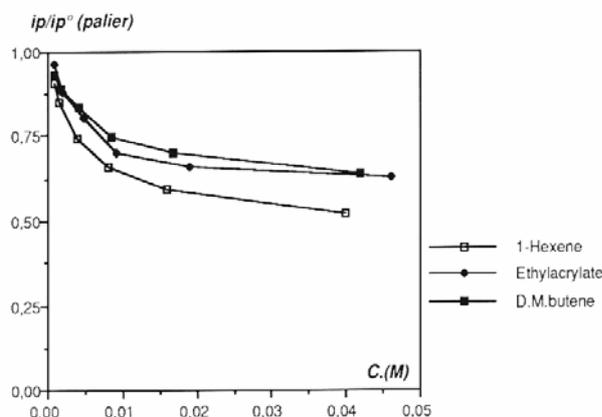
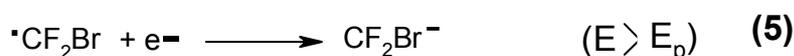
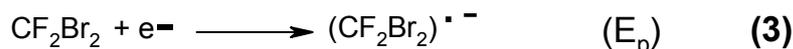


Figure 2b: Superposition $(i_p/i_{p_0})_{palier} = f(\log C)$, C concentration of olefin.

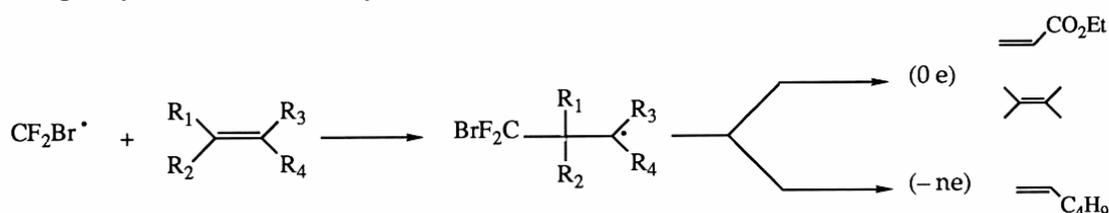
Thus, the variations of i_p / i_{p_0} (i_p : peak current in the presence of olefin; i_{p_0} peak current in the absence of olefin) observed in the presence of ethylacrylate or 2,3-dimethyl-2-butene are almost indistinguishable despite the strong difference of the olefin electronic characters. Also these variations appear to level-off at $i_p / i_{p_0} = 0.5$ when the olefin concentration increases. The decrease of i_p / i_{p_0} in the presence of 1-hexene appears to be slightly faster and, it is noteworthy, reaches values below 0.5. However, no limiting asymptote could be observed in this case, since this would require the use of too large concentrations of olefin for meaningful results to be obtained. Although at this stage, it is impossible to precise the mechanism(s) involved, the above behaviors indicate that the olefin presence results in a disruption of the initial ECE-like reduction sequence (equations 3-6) of CF_2Br_2 by scavenging of one of the four intermediates operative: the anion radical $(CF_2Br_2)^{\cdot -}$, the radical CF_2Br^{\cdot} , the carbanion CF_2Br^- , or the carbene $:CF_2$. A prime involvement of either CF_2Br^- or $:CF_2$ can be easily ruled out since this would not change the number of electron exchanged at the reduction peak of CF_2Br_2 . A chemical reaction between the olefins and the anion radical $(CF_2Br_2)^{\cdot -}$ appears unreasonable based on chemical grounds. At this stage, we are then led to consider that the olefins interfere in the initial reduction sequence at the level of the radical CF_2Br^{\cdot} :



thus preventing its reduction at the electrode surface. Such a kinetic sequence is in qualitative agreement with all the above voltammetric observations. In particular it explains the independence of i_p / i_{p_0} with the scan rate while a dependence is observed with the olefin concentration. Indeed, as established previously, a competition between reduction of the radical (equation 5) and its trapping in equation 13, is primarily function of the ratio $\sigma = k_1 [\text{olefin}] / k_0$, where k_0 is the rate constant of the radical formation (equation 4):

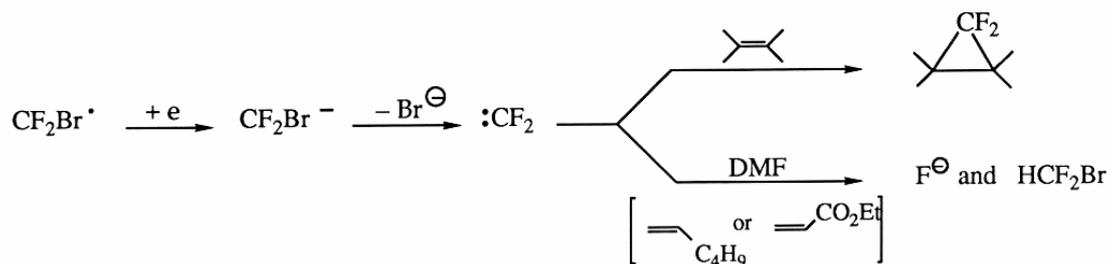


Interestingly, the almost identical variations observed for ethylacrylate and 2,3-dimethyl-2-butene suggest that the corresponding values of k_1 are very close for the two olefins. Owing to their expected strong difference of reactivity *vis a vis* the electrophilic fluorinated radical, this implies that the reactions in equation 13 are diffusion controlled or close to diffusion control. In this respect, it would be surprising that 1-hexene may result in a faster reaction (*viz.* in smaller values of i_p/i_{p_0} for identical concentrations of olefins) than those of ethylacrylate or of 2,3-dimethyl-2-butene as suggested from the results in Figure 2. We are therefore led to conclude that the smaller values of i_p/i_{p_0} observed for 1-hexene do not originate from an important difference of the corresponding rate constants k_1 , but rather stem from a different fate of the radical adduct formed in equation 13. This is in fact compatible with our previous observation that the current ratio i_p/i_{p_0} reaches an horizontal asymptote at 0.5 in the presence of large concentrations of ethylacrylate or of 2,3-dimethyl-2-butene, while it goes below this value for 1-hexene. Such an important difference indicate that in the case of ethylacrylate or of 2,3-dimethyl-2-butene, the radical adducts formed in equation 13 do not lead to further electron transfers, while that formed in the case of 1-hexene leads at least partly to an electrocatalytic mechanism, as summarized in Scheme 1:



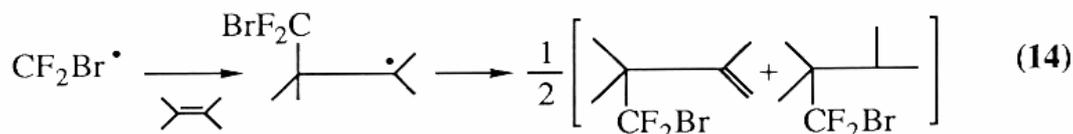
Scheme 1

To substantiate quantitatively all the above qualitative kinetic deductions it is therefore necessary to precise the fate of the radical adducts formed in reactions 13. This can be performed through analysis of products distributions in preparative scale electrolysis. Tables 2 - 4 (see experimental part - preparative electrolyses) indicate that each olefin leads to different product distribution. Except for 2,3-dimethyl-2-butene, one observes product (*viz.* fluoride ions and HCF_2Br) of the initial reduction mechanism (equations 3-6; compare Table 1) together with products related to the olefin yet no cyclopropanation. For 2,3-dimethyl-2-butene fluoride ions and HCF_2Br productions are completely suppressed while cyclopropanation occurs to a large extent. This observation validates indirectly our previous proposal that fluoride ions and HCF_2Br are related to further evolution of electrogenerated difluorocarbenes (equations 9 - 11) in the presence of DMF. In the presence of the electron-rich 2,3-dimethyl-2-butene, difluorocarbenes are indeed expected to react primarily by addition to the olefin instead of reacting with DMF, thus suppressing the formation of fluoride ions (equations 9, 10) and of HCF_2Br (equation 11), while it is reasonable that reaction with DMF is still favored in the presence of the less electron-rich 1-hexene and ethylacrylate (Scheme 2). The other products observed in each case reflect the fate of the adduct of the radical CF_2Br^\bullet with the olefin (equation 13).

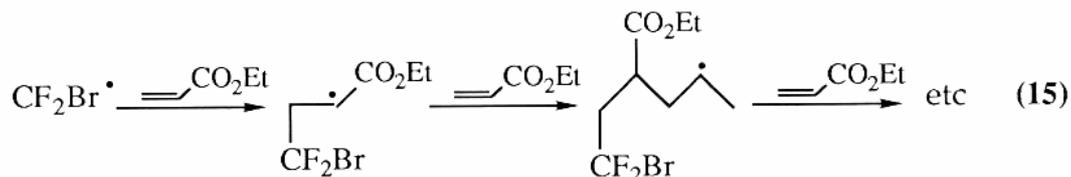


Scheme 2

Thus for 2,3-dimethyl-2-butene one observes a dismutation of the radical adducts (equation 14):

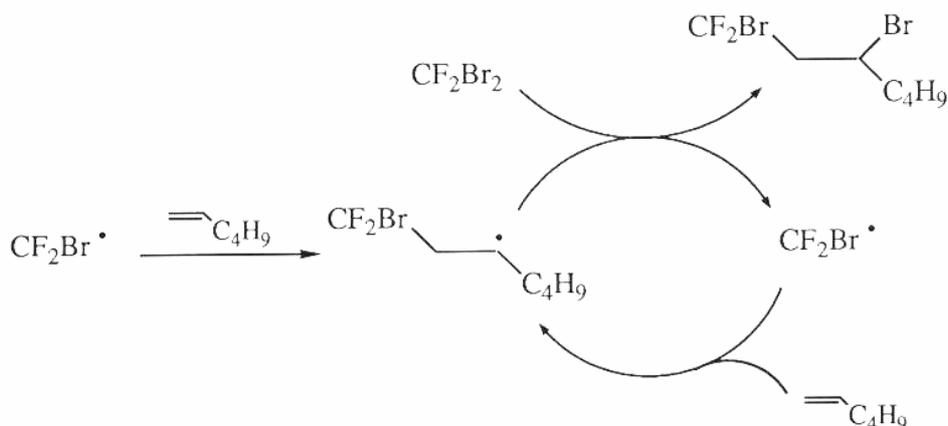


while for the activated ethyl acrylate radical polymerization of the olefin occurs instead (equation 15):



It is worth to emphasize that both reaction pathways involve no further electron transfer or other molecules of CF_2Br_2 , and correspond thus to the kinetic requirement in Scheme 1. Thus the overall number of electrons exchanged in the reduction of CF_2Br_2 in the presence of both olefins is expected to be comprised between 2 (*viz.* when reduction dominates: $k_0 \gg k_1$ [olefin]) and 1 (*viz.* when radical addition dominates: $k_0 \ll k_1$ [olefin]) as observed in cyclic voltammetry (Figure 2). This situation is in strong contrast with that observed for 1-hexene. Indeed, it is seen in Table 4, that the adduct formed in equation 13 evolves mainly to afford $\text{BrF}_2\text{C}-\text{CH}_2-\text{CHBr}-\text{C}_4\text{H}_9$, *viz.* abstracts a bromine atom. Would the source of this bromine atom be the radical $\text{CF}_2\text{Br}^\bullet$ or the anion radical $(\text{CF}_2\text{Br}_2)^\ominus$ one would expect the yields in products from carbene evolution (i.e. F and HCF_2Br) to increase while electrolysis proceeds, in parallel with the increasing yield of $\text{BrF}_2\text{C}-\text{CH}_2-\text{CHBr}-\text{C}_4\text{H}_9$. We are therefore led to conclude that the source of bromine atom is CF_2Br_2 , thus resulting in activation of a non-electron consuming radical chain (Scheme 3).

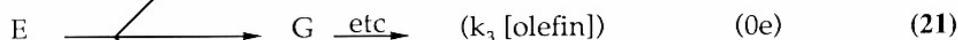
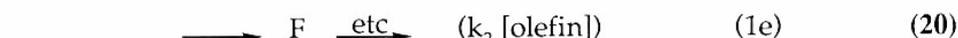
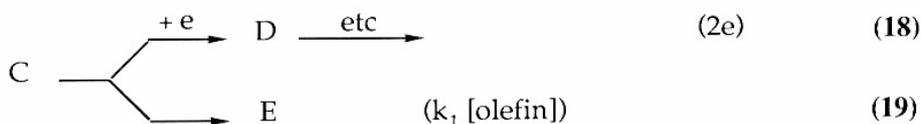
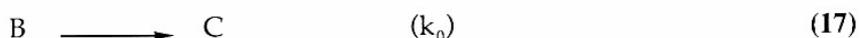
Involvement of the radical chain in Scheme 3 corresponds to the occurrence of an electrocatalytic process, in agreement with the requirement in Scheme 1 and with our voltammetric observation that for 1-hexene i_p / i_{p_0} ratios are smaller than for the two other olefins and reach values below 0.5 at large olefin concentrations.



Scheme 3

QUANTITATIVE KINETIC INVESTIGATION OF THE MECHANISM OF CF_2Br_2 REDUCTION IN THE PRESENCE OF OLEFINS

Based on the above results and discussion, one may propose the general mechanism in Scheme 4 to describe the reduction of CF_2Br_2 in the presence of olefins.



Scheme 4

The overall number of electron consumed in cyclic voltammetry is then determined by the probabilities that each individual route is followed times the number of electron consumed in each route. The two-electron route (reactions 16 -18) is followed with a probability $(1 + \sqrt{\sigma})^{-1}$ i.e : $1/[1 + (k_1 [\text{Olefin}] / k_0)^{1/2}]$, while that leading to the radical adduct is given by $\sqrt{\sigma} / (1 + \sqrt{\sigma})$. The number of electrons consumed along the sequence opened by reaction 19 depends on the probability that each of reactions 20 (1 e overall), 21 (1 e overall) or 22 (1 e overall) is occurring. A general competition between these three paths could be derived by analogy with former work of this group. However, this would lead to a rather complicated kinetic treatment because of the second order character of the dismutation reaction in equation 22. However, noting that

this step occurs only in the case of 2,3-dimethyl-2-butene and then that it occurs exclusively, a simplified kinetic treatment can be proposed by considering only equations 20 and 21. Then the probability that equation 20 (*viz.* the 1e overall route) is followed, is readily given by:

$$\frac{k_1[\text{Olefin}]}{k_2[\text{Olefin}]} + k_3[\text{CF}_2\text{Br}_2] = \frac{\rho}{1 + \rho} \quad \text{with: } \rho = \frac{k_2[\text{Olefin}]}{k_3[\text{CF}_2\text{Br}_2]}$$

while the probability that the 0 electron route is followed (i.e. that initiated by equation 21) is the complementary.

Thus, the overall number of electron exchanged for the sequence in scheme 4 (with exclusion of equation 22) is:

$$n = (2) \times \frac{1}{1 + \sqrt{\sigma}} + \frac{\sqrt{\sigma}}{1 + \sqrt{\sigma}} \left[(1) \times \frac{\rho}{1 + \rho} + (0) \times \frac{1}{1 + \rho} \right] \quad (23)$$

$$\text{i.e.: } n = 2 - \frac{\sqrt{\sigma}}{1 + \sqrt{\sigma}} \left(2 - \frac{\rho}{1 + \rho} \right)$$

$$\text{note that: } \left(\frac{1}{1 + \sqrt{\sigma}} = 1 - \frac{\sqrt{\sigma}}{1 + \sqrt{\sigma}} \right)$$

$$\text{i.e.: } n = 2 - \frac{\sqrt{\sigma}}{1 + \sqrt{\sigma}} \frac{2 + \rho}{1 + \rho} \quad (24)$$

Note that this equation applies also to the case of 2,3-dimethyl-2-butene, i.e. when equation 23 is the main path followed in the sequence 20 - 22, since then it corresponds to $\rho \rightarrow \infty$. Thus equation 24 may be used here to describe all cases at hand. Variations of *n* as a function of $\sigma = k_1[\text{Olefin}] / k_0$ for several values of $\rho = k_2[\text{olefin}] / k_3[\text{CF}_2\text{Br}_2]_0$ are shown in Figure 3.

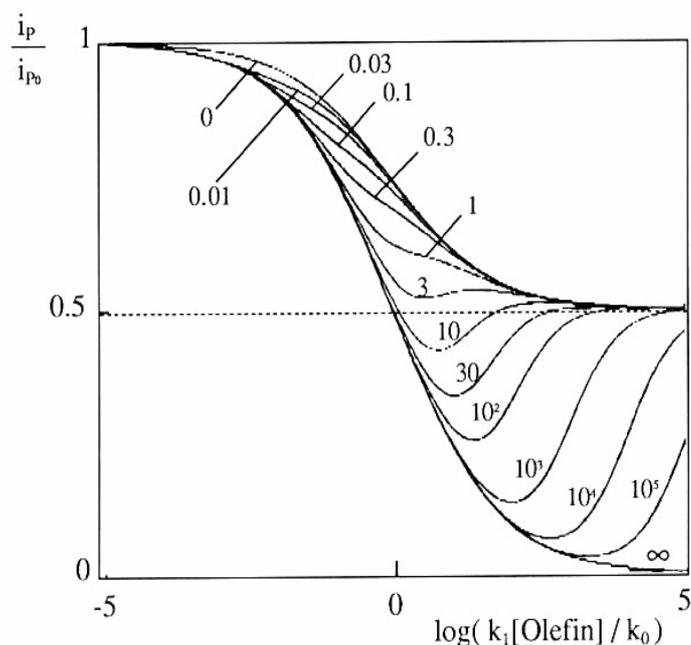


Figure 3. Variation of *n* as a function of σ

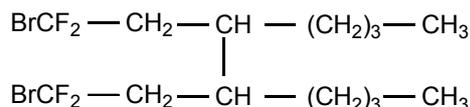
EXPERIMENTAL PART

Preparative electrolysis

The cell used has a cylindrical geometry with a vertical axis. Anodic and cathodic compartments are separated by a fritted glass, porosity n° 4. The cathodic one located in the lower part has a volume of 70 cm³ and the anodic 15 cm³. Electrodes are constituted of carbon cloth (Carbone Lorraine), cathode having an area of 28 cm². Experiments are realized at 0 °C, the cell being partly immersed in an ice bath. The solvent used DMF, from Aldrich, is used directly with a supporting salt: LiCl 0.5M. Potentiostat (used as galvanostat) is a PJT 30-2 from Tacussel.

Electrolysis of CF₂Br₂ in the presence of 1-hexene (Table 1)

Catholyte is charged with 7 cm³ (16.1 g; 77 mM) of CF₂Br₂ and 10 cm³ (6.8 g; 80 mM) of 1-hexene, and 30 cm³ of DMF -LiCl 0.5M. Anolyte is charged with 15 cm³ of DMF -LiCl 0.5M. The cell is maintained at 0 °C by immersion in an ice bath. A constant current (100 mA) is applied to the cell. The composition of the catholyte is followed by ¹⁹F NMR. To samples of 0.3 cm³, are added 10 µl of ϕ CF₃ or C₆F₆, in order to obtain quantitative information. Anolyte is analyzed in the same way, in order to take in account compounds which have diffused in this compartment. The electrolysis is stopped after only a partial consumption of starting material. Spectra recorded indicate the presence of CF₂BrH, a low boiling point compound (b.p. -14°C) [1], which is correctly stored in DMF at 0°C, (CF₂BrH: ¹⁹F NMR: doublet -69.7; -70.7 ppm / CCl₃F; J_{FH} = 63 Hz [2]) Starting CF₂Br₂ is detected at + 3 ppm. Fluorides are present as a singlet at -180 ppm / CCl₃F [2, 3]. The addition compound gives a sharp peak at -45.3 ppm / CCl₃F with small other signals in this part of the spectra (see below). At the end of the electrolysis, the cathodic compartment is filled in 40 cm³ of cold water. This phase is extracted with 3 x 40 cm³ of Et₂O. The ethereal phases are mixed and dried over Na₂SO₄. After filtration, Et₂O is eliminated by slow distillation at atmospheric pressure. The obtained phase is then distilled in vacuum. 5.1 g are obtained at 37 °C under 1.2 mm Hg, corresponding to BrCF₂-CH₂-CHBr-(CH₂)₃-CH₃. ¹⁹F NMR: fine triplet at -43.4 ppm / CCl₃F ; ¹H NMR: 4.2 ppm (q, 1H) CHBr, J_{HH} = 6Hz, 3 ppm (m, 2H) -CH₂- , isolated; 0.8 -2 ppm (m, 9H) CH₃(CH₂)₃ . ¹H NMR data are in accordance with the literature [3], ¹⁹F NMR spectra has not been previously reported. The 5.1 g collected are corresponding with 43 mole % of the CF₂Br₂ converted, the ¹⁹F NMR analysis of the catholyte before extraction was indicating 61% of CF₂Br₂ converted in the addition compound. The efficiency of the extraction and distillation operations seems correct. At the end of the distillation, a residue is observed which has not been analyzed unequivocally, owing to its low mass, but which could be attributed to a dimeric form:



CF₂BrH and unconverted starting CF₂Br₂, present at the end of the electrolysis have been extracted with Et₂O. Thus a part of CF₂Br₂ is observed in the liquid nitrogen trap of the vacuum pump, used in the distillation operation.

Table 1: Reduction of CF_2Br_2 (7 cm^3 ; $16,1\text{ g}$; 0.077 moles) in presence of 1-hexene (10 cm^3 , 0.080 moles), solvent DMF - LiCl 0.5 M , catholytes 30 cm^3 , anolyte 15 cm^3 , constant applied current : 100 mA . Carbon cloth electrodes (cathode 28 cm^2), experiment at $0\text{ }^\circ\text{C}$. Ohmic drop during the operation: 10 Volts

| | | | |
|--------------------------------------|------|------|------|
| Time of electrolysis, hours | 3.5 | 5 | 7 |
| Faradays/mole of starting CF_2Br_2 | 0.17 | 0.24 | 0.34 |
| % of starting CF_2Br_2 consumed | 12 | 34 | 43 |
| Faradays/mole of CF_2Br_2 consumed | 1.41 | 0.75 | 0.79 |
| * $CF_2Br-CH_2-CHBr-C_4H_9$ (mole %) | 38 | 54 | 61 |
| * Fluorides F^- (mole %) | 35 | 24 | 21 |
| * CF_2BrH (mole %) | 24 | 18 | 16 |
| * Other compounds (see text) | 03 | 04 | 04 |

*Products referred to CF_2Br_2 consumed

Electrolysis of CF_2Br_2 in the presence of 2,3-dimethyl-2-butene (Table 2)

5.9 cm^3 (13.6 g , 64 mmole) of CF_2Br_2 and 10.6 cm^3 (7.6 g , 90 mmole) of 2,3- dimethyl-2-butene was added to 35 cm^3 DMF-LiCl 0.3 M in catholyte compartment. Anolyte is charged with 15 cm^3 of DMF-LiCl 0.5 M . In the course of reaction, the cell is maintained at 0°C , by immersion in an ice bath. A constant current (200 mA) is applied. Composition of the catholyte is followed by ^{19}F NMR. 0.3 cm^3 analysis of samples of $10\text{ }\mu\text{l}$ of ϕCF_3 was added in order to obtain quantitative data. Spectra show essentially the presence of three compounds **A**, **B** and **C**.

Table 2: Electrolysis of CF_2Br_2 (5.9 cm^3 ; $13,6\text{ g}$; 64 mmoles) in DMF - LiCl 0.5 M (catholyte 35 cm^3 , anolyte 15 cm^3) in the presence of 2,3-dimethyl-2-butene (10.6 cm^3 , 7.6 g , 90 mmoles), at $0\text{ }^\circ\text{C}$, constant applied current : 200 mA . Carbon cloth electrodes (cathode 28 cm^2)

| | | | |
|--------------------------------------|------|------|------|
| Time of electrolysis, hours | 2 | 4 | 6.5 |
| Faradays/mole of starting CF_2Br_2 | 0.24 | 0.48 | 0.78 |
| % of starting CF_2Br_2 consumed | 15 | 28 | 43 |
| Faradays/mole of CF_2Br_2 consumed | 1.6 | 1.6 | 1.8 |
| * Compound A (mole %) | 53 | 42 | 40 |
| * Compound B (mole %) | 20 | 22 | 23 |
| * Compound C (mole %) | 20 | 22 | 23 |
| * Others (unassigned) (mole %) | 07 | 08 | 10 |
| * Unrecovered CF_2 (mole %) | 00 | 06 | 04 |

*Products referred to CF_2Br_2 consumed

A singlet at $-148\text{ ppm}/CFCl_3$; gem-difluorocyclopropane **A**, resulting from addition of carbene to riche electron olefin, in good yield (40%). The two others products were in 15% yield, at respectively -51.5 ppm and -47.5 ppm / $CFCl_3$, and are attributed to $CF_2Br(CH_3)_2C-C(CH_3)=CH_2$: **B** and $CF_2Br(CH_3)_2C-CH(CH_3)_2$: **C**. At the end of electrolysis, the cathodic compartment is filled in 40 cm^3 of cold water, and then extracted with $3 \times 40\text{ cm}^3$ of Et_2O . The ethereal phases are mixed and dried over Na_2SO_4 . After filtration, Et_2O is eliminated by slow distillation at atmospheric pressure.

The obtained phase is then distilled in vacuum. 2.7 g (36 mol %, on the basis of CF_2Br_2 consumed, a value is in accordance with the NMR yield, table 3, 40 %), colorless liquid was got at 75 °C under atmospheric pressure, attributed to the difluorocyclopropane (compound A), ^1H NMR (TMS) : 1.09 ppm (t), $J_{\text{FH}} = 2$ Hz, $m/e = 134$. Compounds B and C are recovered in the bottom of the distillation.

Electrolysis of CF_2Br_2 in the presence of ethylacrylate (Table 3)

The cathodic compartment is charged with 5.3 cm^3 (12.5 g, 60 mM) of CF_2Br_2 , 15 cm^3 (13.9 g, 138 mM) of ethylacrylate, and 40 cm^3 DMF-LiCl 0.5M. Anolyte is charged with 15 cm^3 DMF-LiCl 0.5M. Experiment is realized at 0°C. A constant current (300 mA) is applied to the cell. Quantitative information is obtained by direct ^{19}F NMR (samples of 0.3 cm^3 with 10 μl of ϕCF_3). The result of the experiment is resumed in Table 3.

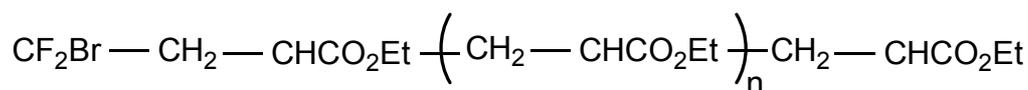
Table 3: Electrolysis of CF_2Br_2 in the presence of ethylacrylate. Catholyte CF_2Br_2 5.3 cm^3 (12.5 g, 60 mM), $\text{CH}_2=\text{CH}-\text{CO}_2\text{Et}$ 15 cm^3 (13.9 g, 138 mM), DMF-LiCl 0.5M : 40 cm^3 . Anolyte DMF-LiCl 0.5M : 15 cm^3 . Experiment at 0 °C. Applied current: 300mA. Cathode: carbon cloth 28 cm^2

| Time of electrolysis, hours | 1 | 2 | 3.5 | 5 |
|--|--------|------|------|------|
| Faradays/mole of starting CF_2Br_2 | 0.19 | 0.37 | 0.65 | 0.93 |
| % of starting CF_2Br_2 consumed | 25 | 45 | 72 | 98 |
| Faradays/mole of CF_2Br_2 consumed | 0.76 | 0.80 | 0.90 | 0.95 |
| * Oligomers (mole %) | 48 | 45 | 48 | 54 |
| * CF_2BrH (mole %) | 48 | 39 | 33 | 19 |
| * Fluorides, F^- (mole %) | traces | 10 | 12 | 18 |
| * Unrecovered CF_2 (mole %) | 05 | 05 | 07 | 08 |

* mole % of CF_2Br_2 consumed

Analysis of ^{19}F NMR spectra shown the presence of CF_2BrH , represented by a doublet at -69,7 and -70,7 ppm / CCl_3F , and fluorides recognized by a singlet at -180 ppm / CCl_3F . Around -45 ppm / CCl_3F , a large peak is present, attributed to the oligomers product.

Cathodic compartment is filled in 40 cm^3 of cold water. This phase is extracted with 3 x 40 cm^3 of Et_2O . The ethereal phases are mixed and dried over Na_2SO_4 . After filtration, Et_2O is eliminated by slow distillation at atmospheric pressure. The obtained phase is then distilled under reduced pressure. After extraction, distillation gives a fraction 80 - 112 °C under 1 mm Hg (4.1 g, 33 %), two fractions until 72 °C. ^1H and ^{19}F spectra are complex. After addition of ϕCF_3 , it has been possible to conclude to the presence of oligomers of general formula:



with a mean value $n = 2$, on the basis of ^1H and ^{19}F data. The bottom of distillation (1.8 g) can be attributed to higher oligomers.

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