

ELECTROCHEMICAL REDUCTION OF CF_2Br_2 ALONE. NUMBER OF ELECTRONS CONSUMED

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Abstract: Electrochemical reduction of CF_2Br_2 alone is investigated in DMF. In the absence of an added olefin, the reduction occurs via an overall two-electron ECEC process that proceeds through the intermediary formation of $\text{CF}_2\text{Br}^\cdot$, $\text{CF}_2\text{Br}^\cdot$ and $\text{CF}_2\text{Br}^\cdot$ that yields ultimately the carbene $:\text{CF}_2$ that reacts with DMF. Also it is possible to determinate the value of the number of electrons consumed directly with the combination of peak current in LSV and limiting current at a rotating disk electrode, we found $n = 2$, we considered the reduction of CF_2Br_2 is bielectronic corresponding to the formation of the methide $\text{CF}_2\text{Br}^\cdot$.

Keywords: *reduction, number of electron, linear sweep voltammetry, glassy carbon cathode, disk electrode*

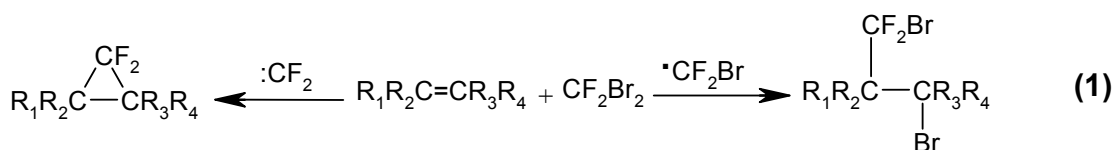
INTRODUCTION

The synthesis of molecules bearing a difluoromethylene group is of general interest [1]. In this perspective, addition of CF_2Br_2 to alkenes appears attractive since it leads generally to bromodifluoromethyl derivatives that may thus undergo further chemical transformations while retaining the grafted CF_2 moiety [2-4]. In the case of electron rich olefins, these reactions are thought to occur via radical chain mechanisms involving homolytic cleavage of one carbon - bromine bond and addition of both the ensuing bromine atom and bromodifluoromethyl radical to the olefin, thus yielding compounds of general formula $\text{BrCF}_2\text{C}-\text{CR}_1\text{R}_2-\text{CR}_3\text{R}_4-\text{Br}$, and are initiated by usual radical promoters (e.g. benzoyl peroxide [5], light [6], $\text{CuCl}/2\text{-aminoethanol}$ [7], BET_3 [8], etc...). Similarly, radical chain addition of polyhalomethanes, and particularly CF_2Br_2 , to olefins through Mn (III) mediated electrochemical initiation has been reported recently [9].

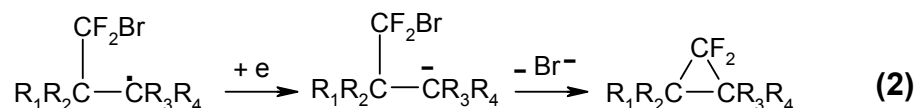
Due to their radical mechanism, these methods are not efficient when electron poor olefins, as ethyl acrylate, enones, acrylonitriles, etc, are concerned. This stems from the general electrophilic character of fluorinated radicals, and so radical polymerisation occurs instead. For such instances, a route based on bimetallic redox system " CrCl_3/Fe " was recently reported [10]. Its mechanism does not appear to involve a simple chain process, since it implies an additional two-electron reduction with respect to $\text{BrCF}_2\text{C}-\text{CR}_1\text{R}_2-\text{CR}_3\text{R}_4-\text{Br}$, indeed, the reaction results in the overall addition of CF_2Br and of an H atom rather than of a bromine atom.

Under truly reductive conditions, an overall cyclopropanation may occur instead. Thus gem-difluorocyclopropanation is reported to take place upon reduction of CF_2Br_2 by metals (Pb [11], Ti (0) [12, 13], Zn [13]) in the presence of adequate olefins. In this respect it is worth to mention that electrochemical reduction of CF_2Br_2 at a platinum electrode has also been reported [11] as an efficient method for cyclopropanation. The reaction is thought to proceed through addition of CF_2 carbenes generated by bromide dissociation from the trihalomethide electrogenerated anion CF_2Br^- , yet, to the best of our knowledge, the involvement of carbenes under both reductive conditions (viz. metal or cathode) has never been established unambiguously (for a discussion of alternative mechanisms yielding to overall cyclopropanations see [14]). Note that the overall gem-difluorocyclopropanations may also be performed through the use of homogeneous organometallic reagents such as $\text{C}_6\text{H}_5\text{-HgCF}_3$ [15a], Me_2SnCF_2 [15b], or with CF_2Br_2 in the presence of triphenylphosphine [15c], or even under phase-transfer catalytic conditions [16].

With exception of these latter conditions which involve organometallic reactions, the above results suggest that radical type reactions [5 - 10] proceed through the intermediate addition of $\text{CF}_2\text{Br}^\cdot$ radicals while under reductive conditions (i.e. in the presence of metals [11-13, 17] or of a cathode [11]) gem-difluorocyclopropanation would occur via carbene addition to the olefin, as is summarized in equation 1.



However, based on a recent study by Wu *et al.* [14], it appears that such a clear-cut dichotomy is too simple. Thus, carbene-like products may be also formed through further evolution of CF₂Br radical adducts to the olefin, albeit the reaction is performed in the presence of zinc metal. This may be rationalized through a possible intramolecular substitution of the bromide ion by the carbanion resulting from reduction of the radical at the metal surface [14]:



However, although the mechanistic sequence in equation 2 seems reasonable, it could not be precised, because of obvious experimental difficulties in executing classical kinetics in the near vicinity of the zinc metal surface.

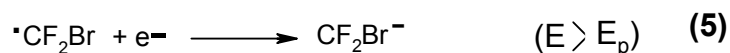
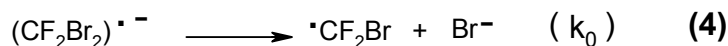
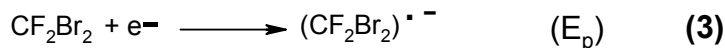
Interestingly, electrochemical methods are perfectly suited for performing kinetic investigations under such micro-heterogeneous localized conditions. This prompted us to undertake a mechanistic study of the reactivity of CF₂Br₂ in the presence of olefins under reductive conditions as provided by a cathode. In the following, we wish to present and discuss the results of such a study.

RESULTS AND DISCUSSION

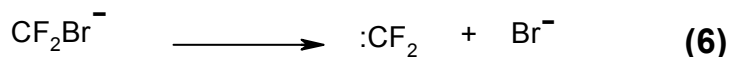
Reduction of CF₂Br₂ alone at a glassy carbon cathode

Cyclic voltammograms of CF₂Br₂ exhibit a single irreversible reduction peak (E_p -1.68 V vs SCE at 0.1 V.s⁻¹; compare Figure 1) resulting in a nearly quantitative formation (i.e. 2 equivalents) of bromide ions as evidenced by the current magnitude of their oxidation peak observed around +1V vs SCE upon scan reversal.

This suggests that the reduction of CF₂Br₂ proceeds through a two-electron ECE-like mechanism, in which reduction of the difluorobromomethyl radical formed upon reductive cleavage following (or possibly concerted with) the initial electron transfer, occurs readily at the peak potential of CF₂Br₂:



possibly followed by dissociation of the trihalomethide anion to afford a difluorocarbene and a bromide ion:



The mechanism in equations 3-6 pre-supposes however several facts that could not be deduced from the straight observation of voltammograms such as those in Figure 1.

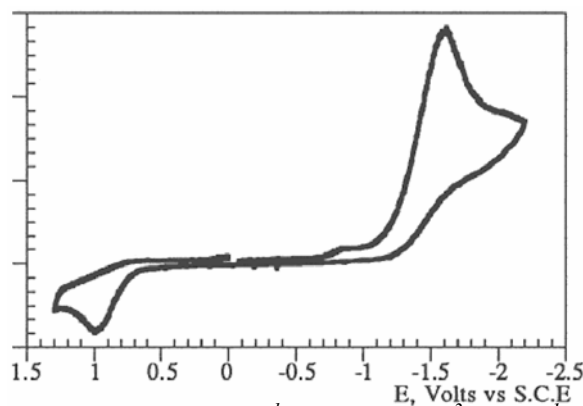


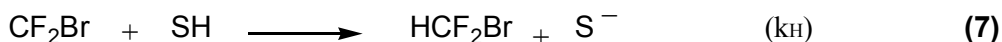
Figure 1 : LSV of CF_2Br_2 : $\nu = 100 \text{ mV} \cdot \text{s}^{-1}$, $C_0 = 3,3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Glassy carbon disk 3 mm in diameter. DMF -TBAF 0.05 M (tetrabutylammonium tetrafluoroborate). Potential referenced to calomel electrode saturated in KCl (SCE). Auxiliary 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.

First it implies an overall number of two electrons exchanged at E_p . Second it involves the intermediacy of an $(\text{CF}_2\text{Br}_2)^{\cdot -}$ anion radical. Third it supposes that the trihalomethyl radical formed by dissociation of the latter is exclusively reduced. Fourth that the ensuing anion formed cleaves off a bromide ion to yield quantitatively a carbene moiety. Let us discuss each of these assumptions in the following.

Point **one** can be established rigorously through the determination of the absolute number of electron involved in voltammetric experiments [18] (see Experimental Section for a description of the method and report of the intermediate results).

Application of this method yields $n = 1.94 \pm 0.05$, in agreement with our above two-electron formulation. Point **two** cannot be established with certainty despite some theories have been proposed in the literature for solving similar problems. Indeed, application of these theories to the case at hand ($\alpha = 0.25$) would lead to the conclusion that steps 3 and 4 should occur in a concerted sequence, without the intermediate formation of a $(\text{CF}_2\text{Br}_2)^{\cdot -}$. Conversely, the formation of this species during reduction of CF_2Br_2 has been evidenced on the basis of the inhibition of its reduction by reducing metals in the presence of *para*-dinitrobenzene [14, 19, 20]. Hence we are inclined to favor the intermediacy of this anion radical. This will be supported by kinetic reasons that will be detailed in the following (*vide infra*).

Point **three**: The reduction in equation 5 may be formally replaced (at least partially) by an alternate route involving an H-atom transfer from the medium (SH) to the trihalomethyl radical, followed by reduction of the radical thus formed:



However several arguments militate against any significant contribution of the route in equations 7, 8 at least under our voltammetric conditions. A sequence such as that in equations 3, 4, 7 and 8 would correspond to the production of only one equivalent of bromide ions in contradiction with the current magnitude of their oxidation wave (compare Figure 1). Also, in the medium used here reduction of the radical S^\cdot has been reported to occur only at potentials more negative than -1.95 V vs SCE [21], i.e; much more negative than E_p (-1.68 V vs SCE in Figure 1); therefore a significant interference of the sequence in equations 7 and 8 would correspond to a number of electron exchanged close to unity, rather than being almost two as determined above. Similarly, the fourth assumption is valid to a large extent: would the trihalomethide anion undergo other routes (e.g. protonation by the medium into HCF_2Br) much less than two equivalents bromide ions would be produced in contradiction with the cyclic voltammetric evidences.

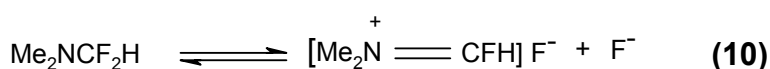
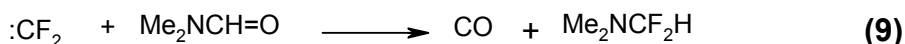
Based on the above results and discussion, it then appears that the sequence in equations 3-6 constitutes an accurate description of the reduction of CF_2Br_2 at a cathode carbon surface, under voltammetric conditions. However, the pertinent rate constants (equations 4 and 6) and standard reduction potential could not be determined because the intrinsic slowness of the electron transfer in equation 3 ($\alpha = 0.25$) prevented the use of fast scan cyclic voltammetry [18], or of redox catalysis [14] for such purposes.

Preparative electrolysis provided similar information for the initial steps of the reduction but in addition allowed to precise the fate of the difluorocarbene generated in equation 6. Indeed, it is noted from the results reported in Table 1 that no tetrafluoroethylene is formed but that fluoride ions are produced in nearly quantitative amounts.

Table 1. Reduction of CF_2Br_2 (5 cm³ ; 11.5 g; 0.055 moles) in DMF -LiCl 0.3 M, catholyte 30 cm³, anolyte 15 cm³. Constant applied current : 100 mA. Carbon cloth electrodes (cathode 28 cm²), experiment at 0°C . Ohmic drop during the operation: 10 Volts. *Products referred to CF_2Br_2 consumed.

Time of electrolysis in hours	2	4	8
Faradays/mole of starting CF_2Br_2	0.135	0.270	0.540
% of starting CF_2Br_2 consumed	7	14	30
Faradays/mole of CF_2Br_2 consumed	1.93	1.92	1.8
* CF_2BrH (mole %)	14 %	21 %	40 %
* F^- (fluorides) (mole %)	86 %	79 %	60 %

This may be rationalized following an initial proposal by Burton *et al.* who have shown that difluorocarbenes are quantitatively trapped by DMF to afford α,α -difluorotrimethylamine which is a good source of fluoride ions [19]:

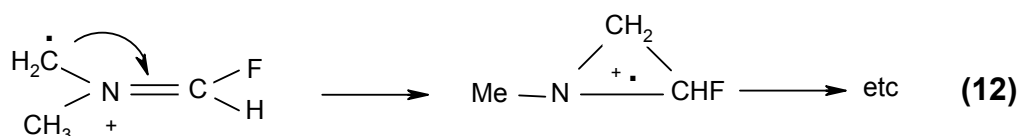


Interestingly, it is noted from Table 1 that while fluoride ions are building into the

electrolytic compartment, one observes a concomitant increase of the yield in HCF_2Br together with a slight decrease of the electron consumption. This may be tentatively rationalized by considering that the imminium cation formed in equation 10 may transfer an H-atom to $\text{CF}_2\text{Br}^\cdot$ radicals before their reduction may occur:



Indeed, the fluoroimminium derivative formed in equation 10 is expected to be a good H-atom donor *via* formation of the corresponding cyclized amminium cation radical. However all our attempts to validate this route by observation of possible follow-up products resulted unsuccessful:



Reduction of CF_2Br_2 at a glassy carbon cathode. Number of electrons consumed

It is possible to obtain the value of n directly through the combination of peak current in LSV, and limiting current at a rotating disk electrode. The method is based on a comparison of the observed currents with the equivalent ones for the oxidation of a compound (here ferrocene), the electrochemical behavior of which is known, in the same medium.

In this way, the number of electrons transferred can be determined without any hypothesis on the value of the diffusion coefficient of the involved species. The oxidation of ferrocene is known as monoelectronic and reversible. Defining i_p as the peak current in LSV, and i_R the current value at a rotating disk electrode, we have:

$$i_p^F = 0.446 F A C_F D_F^{1/2} (Fv / RT)^{1/2} \quad (1)$$

$$i_R^F = 0.620 F A C_F D_F^{2/3} \omega^{1/2} \mu^{-1/6} \quad (2)$$

For ferrocene (reversible system, $n = 1$):

D_F = diffusion coefficient of ferrocene ($\text{cm}^2 \cdot \text{s}^{-1}$);

C_F = concentration of ferrocene in $\text{mol} \cdot \text{l}^{-1}$, A = electrode surface area in cm^2 ;

$R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T in K;

v = scan rate in $\text{V} \cdot \text{s}^{-1}$.

ω = angular velocity in s^{-1} ($\omega = 2\pi f$; f : rotation frequency in $\text{turn} \cdot \text{s}^{-1}$),

F : faradays = 96500 C ,

μ = kinematic viscosity in $\text{cm}^2 \cdot \text{s}^{-1}$ ($\mu = \eta / d$; d : density and η : dynamic viscosity).

For CF₂Br₂ (irreversible system):

D = diffusion coefficient of CF₂Br₂ (cm². s⁻¹) ;

C = concentration in mol.l⁻¹

α = coefficient of electron transfer.

$$i_p = 0.495 n \alpha^{1/2} F A C D (Fv / RT)^{1/2} \quad (3)$$

$$i_R = 0.620 F A C D^{2/3} \omega^{1/2} \mu^{-1/6} \quad (4)$$

From the equations (1) - (4), we obtain:

$$n = \left\{ \left[\frac{0.446}{0.495} \right]^2 \cdot \frac{1}{\alpha} \cdot \left[\frac{i_p}{i_p^F} \right]^2 \cdot \left[\frac{i_R}{i_R^F} \right]^{-3/2} \cdot \left[\frac{C_F}{C} \right]^{1/2} \right\}^2 \quad (5)$$

Experiments in DMF-NBu₄BF₄ 0.05 M at glassy carbon disk 3 mm in diameter, stationary (LSV at 500 mV.s⁻¹) or rotating (500 turn. min⁻¹, scan speed: 100 mV.s⁻¹), give the following values:

$$i_p = 78.4 \mu A, \quad i_p^F = 71.6 \mu A; \quad i_p / i_p^F = 1.095$$

$$i_R = 105.7 \mu A, \quad i_R^F = 53.4 \mu A; \quad i_R / i_R^F = 1.797$$

$$\text{with : } C_F = 1,61.10^{-3} \text{ M}, \quad C = 1,61.10^{-3} \text{ M}; \quad C_F / C = 1.00$$

$$\text{then : } n = 0,122 \cdot 1 / \alpha^2 \quad (6)$$

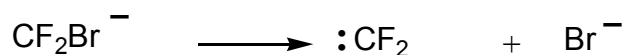
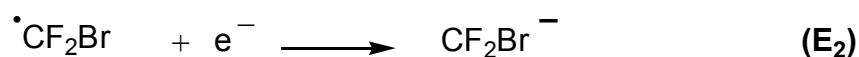
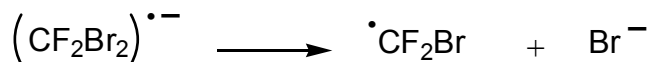
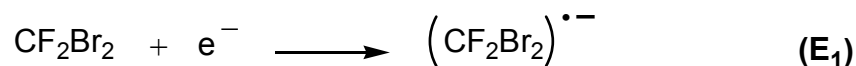
From the voltammogram of CF₂Br₂ we obtain the value of |E_p - E_{p/2}|, where E_{p/2} is the potential at which i = 1/2 i_p, between the starting potential and E_p. We found 190 mV, (voltammogram at 500 mV.s⁻¹). For this measurement, the ohmic drop is exactly compensated, the value of the compensation is chosen in order to observe, for the reversible ferrocene - ferricinium system, a ΔE_p = E_p - E_p of 60 mV, E_p and E_p peak position for the oxidation of ferrocene and the reduction of ferricinium.

For an irreversible system, |E_p - E_{p/2}| is equal to 1.85 RT / α n_a F [21].

So taking T = 298 K:

|E_p - E_{p/2}| = 47.7 / α n_a = 190 mV; n_a is the number of electrons exchanged in the slower step.

On the basis of **scheme A**, the value of n_a can be discussed as follows:



Scheme A

If the overall number **n** of electrons transferred during the reduction of CF_2Br_2 is equal to 1, then n_a is itself necessarily equal to 1. But if $n = 2$, then two values of n_a can be considered:

$n_a = 1$ if the transfer of the first electron at E_1 is slow as compared with the transfer of the second electron (with E_2 equal or more anodic to E_1).

$n_a = 2$ in the reverse case.

The application of the above relationships concludes that the alone possibility is to take $n_a = 1$. Then we obtain $\alpha = 0.251$ and equation (6) gives the overall number of electrons transferred at E_p , $n = 1.94$, therefore **$n = 2$** .

Taking $n_a = 2$, gives $\alpha = 0.125$ and then $n = 7.8$, so this hypothesis has to be discarded. Consequently, we have to consider that the reduction of CF_2Br_2 , at least at the peak potential is bielectronic, corresponding to the formation of the methide CF_2Br^- .

It could be advanced that the reduction of CF_2Br_2 is monoelectronic, yielding the radical $\text{CF}_2\text{Br}^\bullet$ which realize H atom abstraction from the solvent SH (here DMF), yielding S^\bullet . This specie being in turns reduced in S^- . In this way, the reduction would appear as bielectronic. This hypothesis can be clearly discarded, because as established by J.M. Savéant [21], the reduction of S^\bullet in the case of DMF takes place only at a more negative potential (-1.95 V vs SCE).

So, the analysis of the voltammetric pattern leads to consider that the overall number of electron transferred to CF_2Br_2 at E_p is 2, but also that the transfer of the first electron to CF_2Br_2 is slower than the second to CF_2Br . Thus, the consumption of 2 electrons by molecule during the reduction of CF_2Br_2 strongly supports the hypothesis of methide formation, at least in the potential region of the peak.

EXPERIMENTAL PART

Linear Sweep Voltammetry

The cell used with the classical three electrodes arrangement has a volume of 10 cm^3 . The reference electrode, calomel saturated in KCl (SCE), is separated from the solution

by a bridge compartment filled with the same solvent / supporting electrolyte solution as the one used in the cell DMF-NBu₄BF₄ 0.05 M (4 cc). The auxiliary electrode is a platinum sheet 0,2 cm² and the working one is a disk of glassy carbon (Carbone Lorraine), 3 mm in diameter, inserted in a Teflon barrel. Measurements are performed under nitrogen. Voltammograms are recorded in a numerical form, using the Sirius unit from ESII. ¹⁹F and ¹H n.m.r measurements: Spectra are recorded from a Varian EM 360 (56.4 MHz for ¹⁹F; 60 MHz for ¹H).

General procedure consist on the addition of NBu₄BF₄ (0.23 g, 0.05 M) in DMF (14 cc). 4 cc of this solution are introduced in the bridge compartment, and 10 cc in the cell.

Measurements described in the above are conducted with tetrabutylammoniumtetrafluoroborate as supporting salt. For experiments at the preparative level, it is of interest to use LiCl as supporting salt, regarding with the cost and problems concerning the extraction of the products. Consequently, we have determined the peak position for the reduction of CF₂Br₂ in DMF-LiCl 0.2 M. The observed voltammogram is similar with the one when NBu₄BF₄ is the supporting salt: peak potential (at 1 Volt. s⁻¹) is situated at -1.6 Volt/ SCE, with an initial concentration of CF₂Br₂ 2.10⁻³ mol. l⁻¹. The cathodic limit of the system DMF, LiCl is of -2.5 Volt / SCE. However when a higher concentration of CF₂Br₂ is used, and particularly at slow scan rate (0.1 Volt. s⁻¹), the observed peak potential is followed by a plateau with a small distortion at -2.5 Volt / SCE, and the discharge of Li⁺ is rejected at a very negative potential : -3.4 Volt / SCE. A second potential sweep reveals complete blocking of the electrode. It is concluded that an inhibiting film has been formed through which no reduction of CF₂Br₂ is possible.

Similar inhibiting phenomenons have been noticed in a work at platinum electrode in CH₂Cl₂ [17]. These authors remark that alkylammonium salts limitate the phenomenon. Consequently in our preparative experiments we generally chose to work with a constant applied current in the place of the more classical potential controlled techniques.

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