Electrochemical investigation of the redox properties of some polyfluorinated alkenes. The influence of electrode materials on the shape of polarization curves

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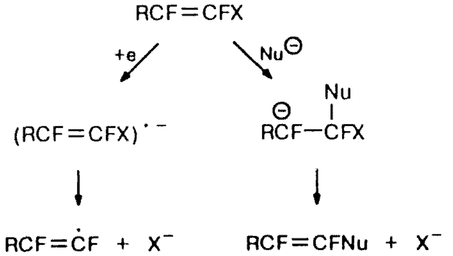
The electrochemical reduction of a number of polyfluorovinyl halides RCF=CFX (R = t-C_4F_9, X = F, Cl, Br; R = Ph, X = F, Cl) has been studied by the cyclic voltammetry technique using various different electrodes. An unusual tendency toward hampering of the reduction was observed on going from X = F to a heavier halogen. Calculations of the energies of the molecular orbitals for these compounds were carried out by the AM1 method. A mechanism of the reduction of polyfluorovinyl halides was suggested on the basis of correlations between the values of the reduction potentials E^{Red} and the LUMO energies.

Key words: polyfluorovinyl halides; cyclic voltammetry; reduction potential, LUMO energy.

RCF=CFX vinyl systems containing fluorine atoms, a nucleophilic group X, and a substituent at the double bond, whose electron acceptor properties can be varied over a wide range are suitable models for studying the regularities of nucleophilic substitution at the alkene carbon atom. Such compounds belong to the class of so-called activated olefins, regardless of the nature of R and X. The alkene can be called activated in reactions of nucleophilic substitution if it has a relatively low lying LUMO. Two fluorine atoms at the double RCF=CFX bond of the molecule are sufficient to fulfill this condition. A more detailed classification can be done. If, for instance, the R group is of the (−M)-type, the alkene is "strongly activated"; however, the alkene is "slightly activated"[1] if R shows no (−M)-properties.

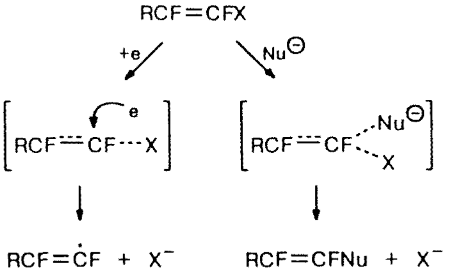
The electron can be considered as the simplest nucleophile; this means that an interior relation should exist between the regularities of the nucleophilic substitution of X in the RCF=CFX molecule and its electrochemical behavior. For instance, if a fairly stable anion radical is formed in electrochemical reduction, nucleophilic substitution is likely to be a "multi-step" process with a carbanion intermediate[1] (Scheme 1).

Scheme 1



On the other hand, if the anion radical is not formed even at high rates of the potential scan, the nucleophilic substitution process is a "single-step" concerted:[1]

Scheme 2



It should be noted that the multi-step mechanism is equivalent to the single-step mechanism when the lifetime of the anion radical tends to zero. Complete analogy between the regioselectivity of the processes of nucleophilic substitution and electrochemical reduction was noticed in the nucleophilic aromatic substitution of polybromobenzenes[2] and anisoles.[3]

The aim of the present work is to study the electrochemical reduction of the series of activated alkenes **1**—**6** shown below:

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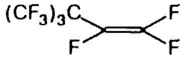
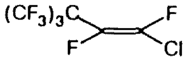
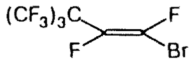


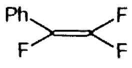
1



***Z*-2**



***Z*-3**



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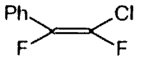
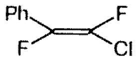


***E*-5**



***Z*-6**

These data are necessary for the investigation of electrochemically activated reactions of nucleophilic substitution in vinyl systems.[4] Additionally, the electrochemical study of the processes proceeding in vinyl halides after the electron transfer to their LUMO makes it possible to simulate the behavior of these compounds in nucleophilic substitution reactions proceeding in solution without any additional external activation.

The cathodic behavior of non-activated vinyl halides has been studied fairly well[5—9] and is almost the same as the behavior of aromatic halides (see Ref. 10 and references cited therein). Usually, a simple scheme is suggested that includes an anion radical whose life time is heavily dependent on the nature of the substrate. It is very short for non-activated substrates and since the vinyl radicals are, as a rule, very easily reduced, a net two-electron process resulting in replacement of halogen by hydrogen is observed:

$$R_2C{=}CRX + e \rightleftharpoons (R_2C{=}CRX)^{\cdot -} \longrightarrow R_2C{=}\dot{C}R + X^-$$

$$R_2C{=}\dot{C}R + e + H^+ \longrightarrow R_2C{=}CHR$$

The stability of the anion radicals increases for perfluoroalkylsubstituted alkenes so they were recently detected by cyclic voltammetry and ESR techniques.[11] The stability of anion radicals and the related degree of reversibility of the reduction of perfluoroethylenes is strongly dependent on the number of perfluoroalkyl substituents as well as on their branching.[11] Reversible reduction was observed for alkenes containing all four perfluoroalkyl substituents when the fluorine atom was one of the substituents. It is likely that reduction became irreversible due to splitting of the fluoride ion from the anion radical.

The electrochemical behavior of a number of halogen derivatives with different halogen atoms at the same vinyl fragment has not been considered until recently.

Experimental

The electrochemical measurements were carried out using a SVA-1B-M voltammetric system with both stationary and rotating platinum (Pt) and mercury film (Hg) electrodes with a working surface of 11.8 mm^2 as well as with a glassy-carbon (GC) electrode with a working surface of 12.56 mm^2 in anhydrous acetonitrile with 0.05 M n-Bu$_4$NBF$_4$ as the supporting electrolyte at 20 °C. In all experiments, platinum served as the auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode.

Acetonitrile of "pure" grade was stirred for 24 h over CaH$_2$ and filtered, then KNO$_3$ (5 g) and conc. H$_2$SO$_4$ (10 mL) were added. The mixture was boiled for 3 h, distilled, boiled again for 2 h over P$_2$O$_5$, and distilled; b.p. 81—82 °C.

The surface of the Pt electrode was coated with a mercury film by means of electrolysis (for 2—3 min) of a $5 \cdot 10^{-4}$ M dibromomercury solution in CH$_3$CN with 0.05 M n-Bu$_4$NBF$_4$ as the supporting electrolyte at the potential corresponding to the limiting current plateau of the reduction of HgBr$_2$ (−0.5 V).

The electrochemical measurements were carried out in a cell 10 mL in volume. Before the experiment, the working Pt electrode was polished with diamond paste and washed with acetone and distilled water. Oxygen was removed from the cell by blowing dry argon.

The concentrations of solutions of the compounds under study were $1 \cdot 10^{-3}$ mol L^{-1}.

The polarization curves were registered by cyclic voltammetry (CVA) at a stationary Pt, GC or Hg electrode at potential scan rates of 50, 100, 200, and 500 mV s^{-1}, and also at a rotating Pt, GC or Hg electrode at 20 mV s^{-1}. The rotation speed of the electrode was varied from 480 to 3450 rev min^{-1}. The ohmic losses were taken into account.

The quantum-chemical calculations were carried out using the semiempirical AM1 method incorporated in the HyperChem Release 3 for Windows molecular design program.

Results and Discussion

1. Using the data of the electrochemical measurements (Table 1, Fig. 1) one can draw the conclusion that the shapes of the polarization curves are strongly dependent on the material of the electrode on which the reduction occurs. The height of the cathodic peak on Pt is always diffusion-controlled since it depends linearly on $v^{1/2}$ (where v is the rate of the potential scan). No anodic peaks were observed (except, perhaps, for compound **6**) when CVA curves on Pt were recorded after passing the cathodic reduction peak and the potential scan to the anodic side (see Fig. 1). This means that the reduction processes of compounds **1**—**6** on the Pt electrode are completely irreversible, both electrochemically and chemically. If, for example, potential scanning toward positive potentials is carried out after the reduction of compound **3**, one can observe peaks of the oxidation of the bromide ion. This means that the starting anion radical decomposes with cleavage of the C—X bond.

Anodic peaks appear on going to Hg and GC electrodes on the back scan of the CVA curves. Their heights depend on the nature of the compound under study and range from 4 to 38 % of the heights of the cathodic peaks (I_p^a/I_p^c = 0.04—0.38). The potential difference $E_p^a - E_p^c$ sometimes appreciably exceeds 58 mV (see Table 1), which is the theoretical value for the thermodi-

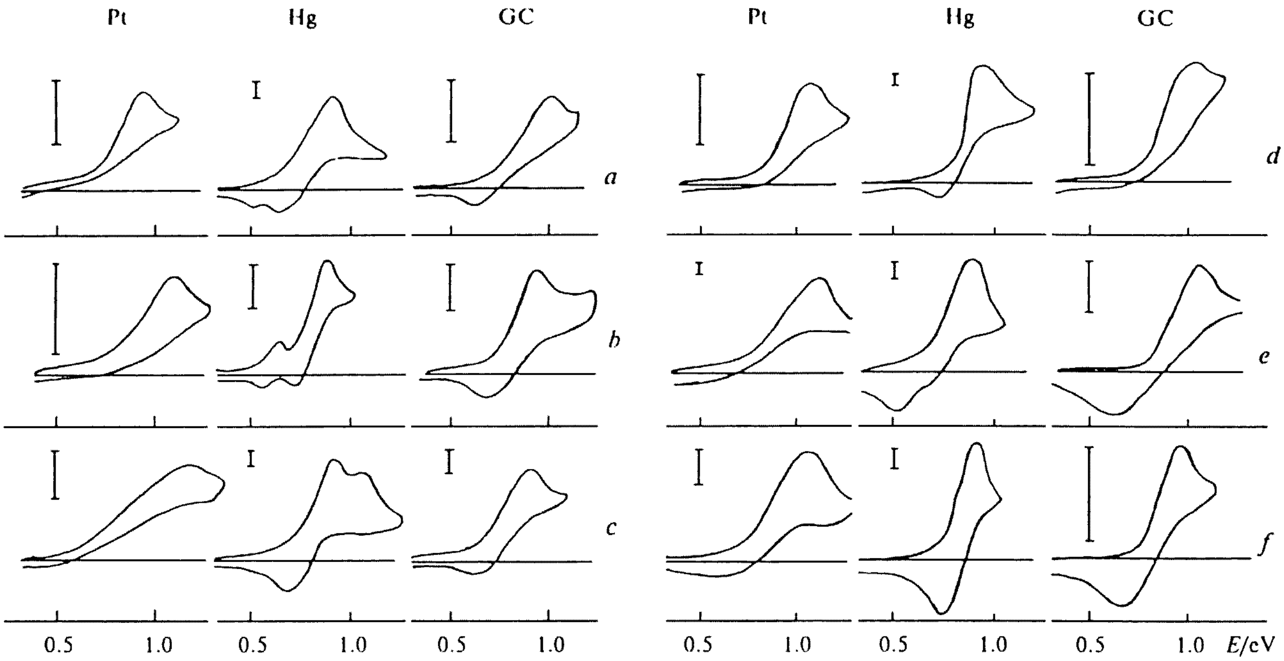


Fig. 1. The effect of the electrode material on the CVA morphology of polyfluorinated alkenes; the concentration in mole L^{-1} is indicated in parentheses: *a*, **1** ($0.67 \cdot 10^{-3}$ (Pt and GC), $1.89 \cdot 10^{-3}$ (Hg)); *b*, **2** ($1.2 \cdot 10^{-3}$); *c*, **3** ($1.0 \cdot 10^{-3}$); *d*, **4** ($1.89 \cdot 10^{-3}$); *e*, **5** ($1.59 \cdot 10^{-3}$); *f*, **6** ($1.7 \cdot 10^{-3}$). The length of the vertical line segment on the diagrams corresponds to the current of 50 μA (CH_3CN, 0.05 *M* *n*-Bu_4NBF_4, Ag/AgCl/KCl, 20 °C, the rate of potential scan: for the curves Hg/*a*, GC/*b*, and Hg/*d* — 500 mV s^{-1}, for the curves Pt/*b*, GC/*d* and GC/*f* — 100 mV s^{-1}, in other cases — 200 mV s^{-1}).

Table 1. Data on the electrochemical reduction of polyfluorovinyl halides RCF=CFX (CH_3CN, 0.05 *M* *n*-Bu_4NBF_4, Ag/AgCl/KCl, 20 °C)

Compound	Pt		GC				Hg			
	n*	$-E^{Red}$/V	$-E^{Red}$/V	v/mV s^{-1}	E^a-E^c/V	i^a/i^c	$-E^{Red}$/V	v/mV s^{-1}	E^a-E^c/V	i^a/i^c
(*Z*)-$C_4F_9{}^tCF=CF_2$	1.32	0.99	0.92	100	0.10	0.01	0.85	100	0.11	0.08
				200	0.13	0.09		200	0.15	0.14
				500	0.15	0.17		500	0.21	0.17
(*Z*)-$C_4F_9{}^tCF=CFCl$	1.33	1.04	1.02	100	—	—	0.86	100	0.12	0.02
				200	0.17	0.04		200	0.17	0.06
				500	0.21	0.10		500	0.23	0.10
(*Z*)-$C_4F_9{}^tCF=CFBr$	1.21	1.17	1.04	100	—	—	0.88	100	0.12	0.10
				200	0.19	0.04		200	0.16	0.19
				500	0.26	0.10		500	0.23	0.21
$PhCF=CF_2$	1.5	1.13	1.05	100	—	—	0.89	100	—	—
				200	—	—		200	—	—
				500	—	—		500	0.22	0.04
(*E*)-PhCF=CFCl	1.32	1.12	1.08	100	0.42	0.19	0.87	100	0.16	0.13
				200	0.51	0.17		200	0.18	0.17
				500	0.64	0.19		500	0.24	0.30
(*Z*)-PhCF=CFCl	1.00	1.15	1.08	100	0.24	0.25	0.86	100	0.10	0.34
				200	0.30	0.22		200	0.12	0.38
				500	0.40	0.25		500	0.20	0.38

* *n* — The electron number (data for the Pt electrode).

namically reversible (completely reversible) process. In that case the cathodic peaks at Hg and GC electrodes and at the Pt electrode are diffusion peaks and correspond to (1.3—1.5) electrons. Two assumptions can be made: either the processes on Hg and GC electrodes become quasi-reversible (chemically reversible), *i.e.*, the stability of the anion radicals on these electrodes is for some reason greater than that on the Pt electrode, or the anodic peaks do not correspond to anion radicals. They may correspond to other products formed during reduction on the cathodic branch of the CVA curve, which, for some reason, can not be recorded with the Pt electrode.

2. The reduction potential peaks (E^{Red}) weakly depend on the nature of the halogen X in molecules **1—6**, in particular at the Hg cathode. Nevertheless, a tendency toward hampering of RCF=CFX reduction on going from X = F to a heavier halogen is traced. It is particularly noticeable for R = t-C_4F_9 at the Pt electrode.

The F > Cl > Br sequence appears to be very unusual and is not typical for previously studied alkyl and aryl halides. In order to explain the experimental results, it is necessary to consider three factors affecting the value of E^{Red}.

The energetic factor is associated with the LUMO perturbation of the RCF=CFX molecule when passing from X = H to X = Hal. If we assume that the LUMO of these molecules possesses π-symmetry (see below), *i.e.*, is the antibonding orbital of the C=C bond, the perturbation of that π*-level when passing from X = H to X = Hal will be a result of π-interaction of the C=C bond with the unshared electron pair of the substituent X, as well as of the σ-interaction of X with the rest of the molecule. The latter interaction also affects the π-levels of the C=C bond (the inductive effect).

Let us consider the ethylene molecule CH_2=CHX containing a π-donor substituent X with an unshared electron pair (*e.g.* X = F, Cl, Br) in accordance with the previously published work.[12] As usual, we describe the C=C bond by π- and π*-orbitals. For simplicity, we describe the π-donor as having merely one filled φ_D orbital (the unshared pair). Figure 2, *a* shows an example with a low-lying φ_D orbital, which corresponds to a weak donor; the φ_D orbital lies relatively high in Fig. 2, *b* (a strong donor). Applying orbital mixing rules for the case in question (three-orbital interaction) we get the diagrams shown in Fig. 2.

A stronger donor increases the energy of an empty π_3^*-orbital (*i.e.*, destabilizes it) more than a weaker donor; in fact, φ_D is closer in its energy to the ethylene π*-level in the first case than it is in the second. If the principle factor determining the reduction potential is the level of the π_3^*-orbital, the reduction of X must be hindered by introduction of a stronger donor into the molecule (E^{Red} shifts to more negative potentials). In accordance with their π-donor properties (the φ_D orbital level), halogens form the following sequence: Br > Cl > F.

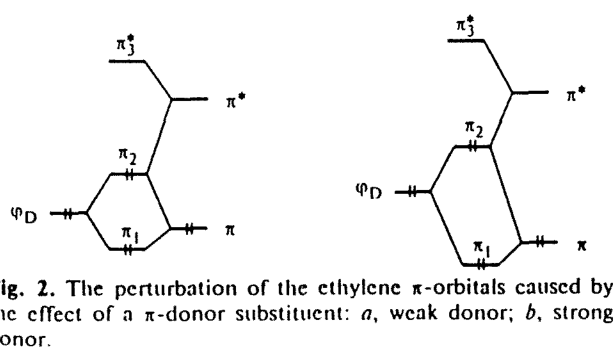


Fig. 2. The perturbation of the ethylene π-orbitals caused by the effect of a π-donor substituent: *a*, weak donor; *b*, strong donor.

The role of the inductive effect is shown in Fig. 3. When an X-substituent with a strong (−*I*)-effect is introduced, a positive charge is generated at the adjacent carbon atom, *i.e.*, its electronegativity increases. As a result, both π-levels of the C=C bond (such as π and π*) get stabilized (see Fig. 3, *b*), or, in other words the C=C→X bond (for example) becomes similar to the carbon—oxygen bond in the carbonyl group, which is characterized by low-lying π- and π*-orbitals. However, an X-substituent with a strong (−*I*)-effect can not simultaneously be a strong π-donor. Hence, elevation of the π and π* levels in the C=C→X molecule is followed by the simultaneous lowering of the π-level of φ_D. In principle, a situation is possible in which the level splitting inside the diagram of the orbital interaction is unchanged on passing from a (+M)-substituent to a (+M, −*I*)-substituent; however, the whole diagram shifts to lower energies, which results in π_3^*-stabilization, *i.e.*, in facilitation of reduction (see Fig. 3).

According to their inductive effect, the halogens are in the sequence F > Cl > Br. Thus, if only energetic reasons are considered without regard for the steric factor, fluorine must destabilize the π_3^*-orbital to a lesser degree according to the π-mechanism and stabilize it to a greater degree in accord with the inductive σ-mechanism. Both energetic factors act in the same direction and must provide this theoretical sequence of increasing reduction capacity: C=CBr < C=CCl < C=CF.

Steric factor. The overlap of the halogen orbitals with the carbon orbitals decreases as the atomic number of the halogen increases due to steric reasons. The orbitals of fluorine, the element of the same period as carbon, overlap better, while the iodine orbitals overlap

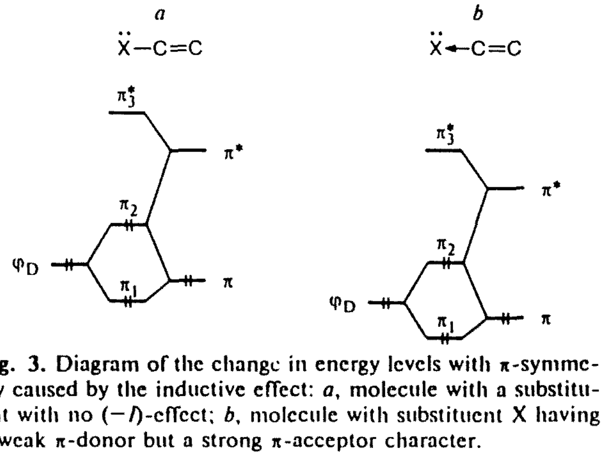


Fig. 3. Diagram of the change in energy levels with π-symmetry caused by the inductive effect: *a*, molecule with a substituent with no (−*I*)-effect; *b*, molecule with substituent X having a weak π-donor but a strong π-acceptor character.

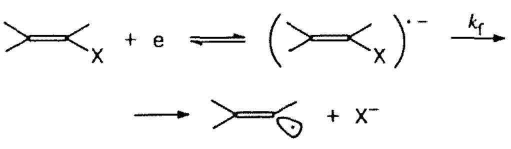
worse than those of the other halogens; this is valid for both π- and σ-overlap. The correlation between the size of the fluorine and carbon orbitals seems to make the π-donor properties of the former stronger (without increasing φ_D), than those of the heavier halogens, resulting in more efficient interaction between φ_D and π^*, which raises the π^*_3 level. Thus, the steric and energetic factors have the opposite effects on the position of the π^*_3 level; the only steric effect with no allowance for energetic factor gives rise to the following sequence of increasing ease of reduction: C=CF < C=CCl < C=CBr, *i.e.*, the usual sequence of the reduction of aromatic halogen derivatives.[13,14]

The role of steric factors is particularly pronounced, if the σ-constants (in the Gammett equation or its modifications) of the halogen atom substituents are compared: almost all σ-constants (except σ_I) in the sequence F, Cl, Br, I become more positive or more negative.[15—19] This means that the π-donor effect for fluorine (as a substituent in the benzene ring) is the largest, while that for iodine is the smallest, *i.e.*, the steric factor dominates over the energetic factor.

Though the σ-constants and relevant conclusions obtained are only for benzene derivatives, it should be noted that a good correlation between the ionization constants of *trans*-3-substituted XCH=CHCOOH acryl acids with the Gammett σ_{para} constants has been observed.[20] It is obvious that in this case, the inductive, resonance, and other effects are mixed nearly in the same proportion as for *para*-substituents in a benzene ring.

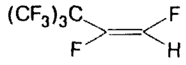
An increase in the steric factor due to σ-overlap results in stronger perturbation; as a result the C—X bond becomes less covalent (less similar to the atomic orbital of the X atom). Hence, like in the case of π-interaction, the increasing overlap weakens the effect of the steric factor, which is associated with the atomic electronegativity of X. In other words, the inductive effect seems to be weakened with increasing overlap.

The kinetic factor. One more parameter affecting the observed potential of the irreversible process of reduction of organic halides is the rate of fragmentation (k_f) of the initially formed anion radical to form the organic radical and the halide ion:

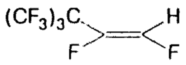


The fragmentation rate increases as the nucleofugacity of the X^- group increases, which corresponds to the halogen sequence $I^- > Br^- > Cl^- > F^-$. The larger k_f is, the more the observed E^{Red} potential shifts from the standard potential value to the less cathodic side. Hence, one can expect that if the difference in the E^0 values is small for the F-, Cl-, Br-, and I-derivatives and the difference in log k_f for halogens is sufficiently large, "the reduction ease" estimated from the observed potential will decrease in the sequence $CH_2=CHI > CH_2=CHBr > CH_2=CHCl > CH_2=CHF$. Thus, the effect of the kinetic factor (as well as that of the steric factor) is opposite to the effect of the energetic factor.

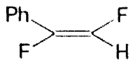
The observed sequence F > Cl > Br, particularly pronounced for compounds **1—3** on the Pt electrode, can be explained by the fact that in this case the E^{Red} value is mostly determined by the energetic factor and not by the steric and kinetic factors. Since the energetic and steric factors are related to the perturbation of molecular orbitals, one can estimate their relative significance by means of quantum-chemical calculations. We carried out semiempirical calculations by the AM1 method with complete optimization of the molecular geometry in order to determine the LUMO energies of compounds **1**, **2**, **4—6** (X = F, Cl) as well as those of related molecules **7—16** (several of which are the reduction products of compounds under study):



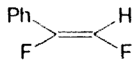
(*E*)-**7**



(*Z*)-**8**



(*E*)-**9**



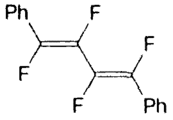
(*Z*)-**10**

$(CF_3)_3CC{\equiv}CF$

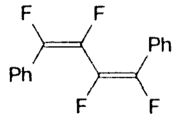
11

$PhC{\equiv}CF$

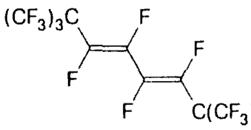
12



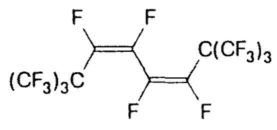
(*E,E*)-**13**



(*Z,Z*)-**14**



(*E,E*)-**15**



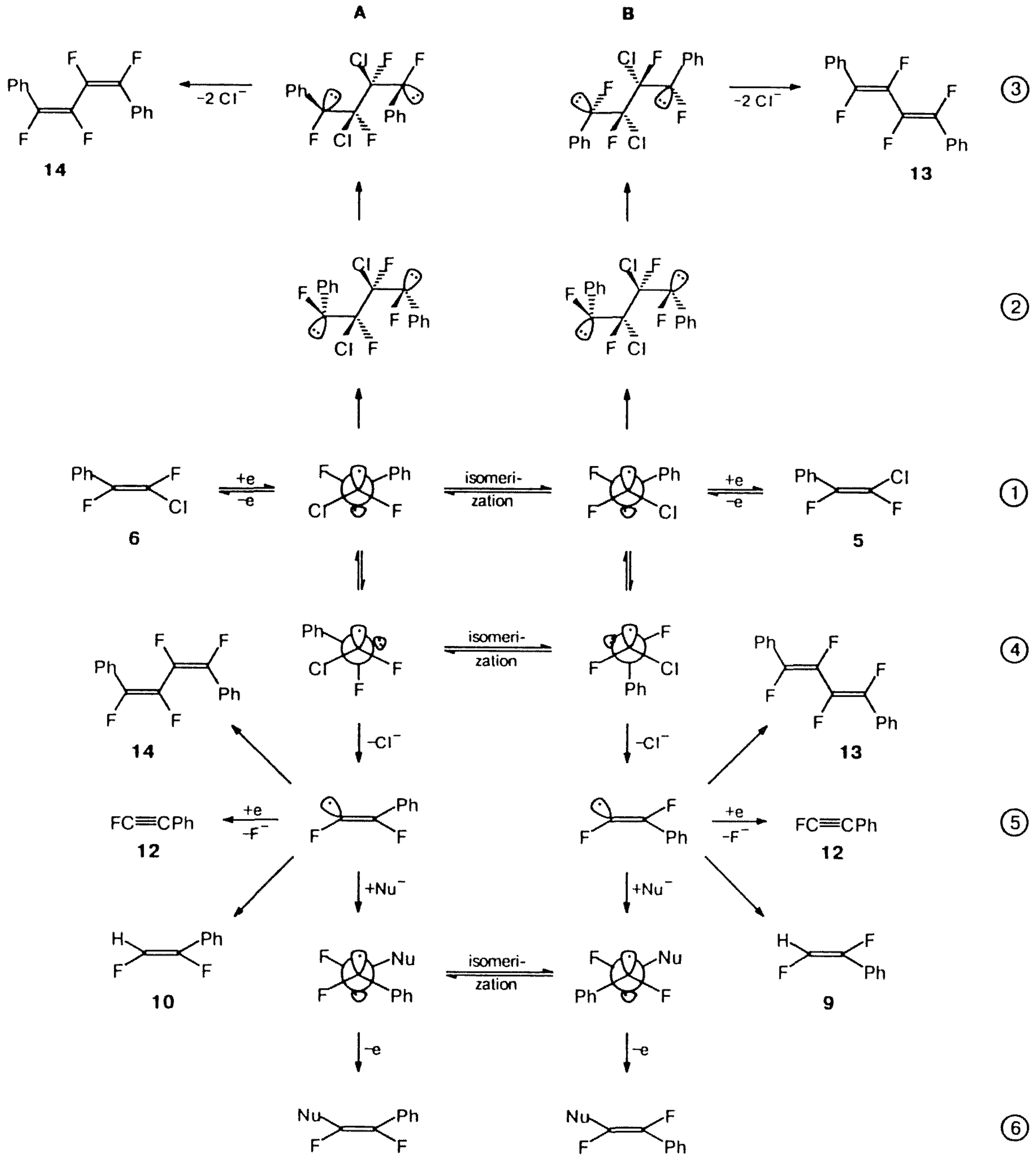
(*Z,Z*)-**16**

These products can be formed in the process of electrochemical reduction as was exemplified by difluorostyrenes **5** and **6** (Scheme 3).

The following assumptions were made when composing Scheme 3. The electron transfer occurs to the π*-LUMO of the C=C bond with the formation of the anion radicals, which can be considered as an antiperiplanar species if their structures are conditionally written as those of ketyl radicals

$$(\gt\dot{C}-O^-)\,.$$

Scheme 3



Anion radicals $5^{\cdot-}$ and $6^{\cdot-}$ can enter the *cis-trans*-isomerization reaction since their C=C bonds are weakened. Such isomerizations reactions are known in the literature.[5,9] The elimination of the halide ion occurs after adoption of the synclinal conformations $5^{\cdot-}$ and $6^{\cdot-}$ by the anion radical, since in this case the chlorine adopts the antiperiplanar position with respect to the orbital bearing the carbanion negative charge, and favorable *trans*-elimination is possible. The vinyl carbanions and radicals are sufficiently stable configurationally.

In Scheme 3, reaction (1) is the initial process of the reduction of compounds 5 and 6 and of the isomerization of the anion radicals; **A** and **B** correspond to different isomers; (2) and (3) are the dimerization of anion radicals to dianions and the elimination of two chloride ions from the latter to form (*E,E*)-(**13**) and (*Z,Z*)-(**14**)-isomeric disubstituted butadienes; reactions (4) and (5) are the elimination of the halide ion from the anion radicals $5^{\cdot-}$ and $6^{\cdot-}$ resulting in the formation of vinyl type radicals. The latter can either dimerize

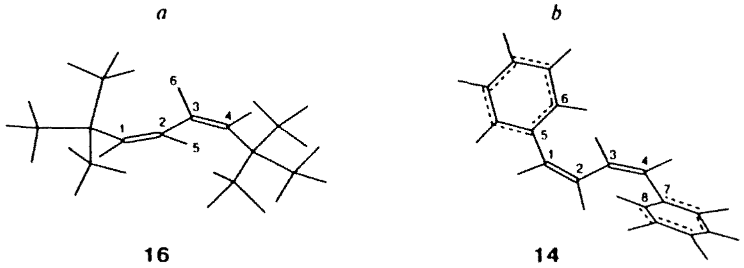
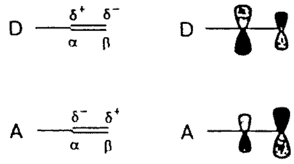


Fig. 4. Spatial structure of (*Z*,*Z*)-isomers of substituted polyfluorobutadienes $(CF_3)_3CCF=CFCF=CFC(CF_3)_3$ (**16**) and PhCF=CFCF=CFPh (**14**).

into dienes **14** and **15** or further reduce to phenylfluoroacetylene **12** (reductive dehalogenation) or to difluorostyrenes **9** and **10**. If a portion of the anion radicals can go from the electrode into solution before decomposing and dissociate in solution, radicals **5**$^\cdot$ and **6**$^\cdot$ can either abstract a hydrogen atom from the solvent molecule to yield **9** and **10** or enter a reaction with nucleophiles (if they are in the solution) to form the product of nucleophilic substitution (6) by the $S_{RN}1$-mechanism.

The AM1 method of optimization of molecular geometry for substituted butadienes **13**—**16** results in planar molecules for (*E*,*E*)-isomers **13** and **15** and in non-planar (*Z*,*Z*)-isomers **14** and **16**. The dihedral angle 1—2—3—4 in molecule **16** is 21°, and 5—2—3—6 angle equals 29° (Fig. 4). Even larger deviations from a planar structure are observed for compound **14**, where the dihedral angle 1—2—3—4 is equal to 40.6°, and the improper torsion angle 5—6—7—8 is 97.6°. The small deviations from planarity of the butadiene π-system have virtually no effect on the energy of the frontier orbitals of isomers **15** (planar) and **16** (nonplanar); however, the large deviations and the loss of conjugation by phenyl groups make the LUMO of isomer **14** much less stable and the HOMO of this isomer more stable than those of the planar isomer **13** (Table 2). As was shown previously,[21] hexafluorobutadiene is also nonplanar and exists as the cisoid conformer with the dihedral angle ~48°. The data on calculations of energies and charges given in Table 2 and Fig. 5 show that for all molecules under study the LUMOs are π* type orbitals, mostly localized on the ethylene fragment (see Fig. 5, *a*). Allowance for configuration interactions does not change the LUMO type, whose population is equal to ~0.03. The HOMOs are bonding π-type orbitals (see Fig. 5, *b*).

In the molecules of alkenes **1**, **7**, and **8**, if R = *t*-C_4F_9, the charge at the C(β) atom is positive, whereas it is negative at the C(α) atom (the charge at the C(β) atom is close to zero and negative at the C(α) atom in the molecule **2**). In contrast to this, the charge is negative at the C(β) atom and positive at the C(α) atom in compounds **5**, **6**, **9**, and **10** (R = Ph). This change in the charge polarization with the change of R (from R = *t*-C_4F_9 to R = Ph) could be related to the π-donor-acceptor properties of the R group. If R is a π-donor (D), the C=C bond is polarized in the opposite direction than that when R is a π-acceptor (A). In accordance with this, the coefficients at C(α) and C(β) in the π*-LUMOs change:



t-C_4F_9 is not a π-donor group and it can be called type A, while the phenyl group is a good donor with respect to the electron deficient C=C bond and belongs to type D. Hence, in the case of R = *t*-C_4F_9 the dipole moment of the C=C bond is directed from C(β) to C(α),

Table 2. Energy and charge characteristics for several polyfluoroalkenes and acetylenes calculated by the AM1 method

Compound	Orbital energies/eV		Charge	
	HOMO	LUMO	C(α)	C(β)
$C_4F_9{}^tCF=CF_2$	−11.70[a] −11.04[b]	−1.71[a] −1.79[b]	−0.088[a] −0.082[b]	+0.239[a] +0.212[b]
(*Z*)-$C_4F_9{}^tCF=CFCl$[b]	−11.89	−1.61	−0.065	−0.007[b]
$PhCF=CF_2$	−9.51	−0.92	+0.046	+0.112
(*E*)-PhCF=CFCl	−9.33	−0.89	+0.072	−0.099
(*Z*)-PhCF=CFCl	−9.25	−0.84	+0.069	−0.104
(*E*)-$C_4F_9{}^tCF=CFH$[b]	−11.60	−1.38	−0.067	+0.073
(*Z*)-$C_4F_9{}^tCF=CFH$[b]	−11.58	−1.40	−0.070	+0.065
(*E*)-PhCF=CFH	−9.37	−0.62	+0.052	−0.049
(*Z*)-PhCF=CFH	−9.41	−0.67	+0.041	−0.047
$C_4F_9{}^tC{\equiv}CF$	−12.60	−0.87	−0.280	+0.160
$PhC{\equiv}CF$	−9.48	−0.26	−0.116	−0.025
(*E*,*E*)-$(PhCF=CF-)_2$	−8.83	−1.45	+0.097	+0.004
(*Z*,*Z*)-$(PhCF=CF-)_2$	−9.31	−1.14	+0.094	+0.008
(*E*,*E*)-$(C_4F_9{}^tCF=CF-)_2$	−11.40	−2.88	+0.015	+0.090
(*Z*,*Z*)-$(C_4F_9{}^tCF=CF-)_2$	−11.49	−2.87	+0.035	+0.084

Note. α-Position corresponds to the carbon atom bonded to R.

[a] Eclipsed conformation.

[b] Staggered conformation.

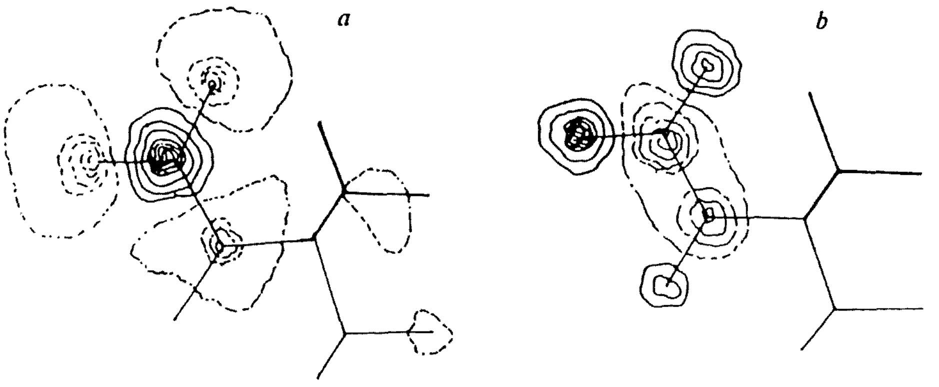
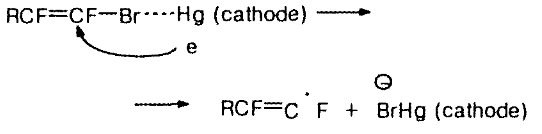


Fig. 5. Cross sections through the frontier orbitals of a $(CF_3)_3CCF=CF_2$ molecule (**1**) calculated by the AM1 method: *a*, LUMO; *b*, HOMO.

while at R = Ph the direction is from C(α) to C(β), which is in agreement with the results of calculations.

The LUMO energies are negative, *i.e.*, all studied compounds have a pronounced electron affinity, which is confirmed by the low values of the reduction electrochemical potentials (E^{Red} in Table 1). A linear correlation between the calculated values of the LUMO energies and the electrochemical potentials is observed: electrochemical reduction becomes easier as the LUMO energies decrease.

The existence of such a correlation allows one to accept the mechanism of the reduction of polyfluorovinyl halides based on the initial formation of the anion radical in the potential-determining step (see Scheme 1). A concerted process of electron transfer with more or less simultaneous cleavage of the C—X bond in the RCF=CFX molecules is highly improbable, since in that case one should expect the inversion of the reactivity sequence (F > Cl > Br ⇢ Br > Cl > F) because the fluoride ion is a very sluggish leaving group. However, the concerted process could be realized on mercury, which, by coordinating with the heavy halogen, facilitates its splitting:



$$\text{RCF=CF—Br}\cdots\text{Hg (cathode)} \xrightarrow{e} \text{RCF=}\dot{\text{C}}\text{ F} + \overset{\ominus}{\text{Br}}\text{Hg (cathode)}$$

It is possible that for this reason the reduction potentials of all studied compounds on the Hg cathode are nearly identical; the catalytic effect of mercury is stronger for a heavier halogen, and due to that the F > Cl > Br sequence turns into F ≈ Cl ≈ Br.

If X = F, Cl is replaced by hydrogen in molecules **1**, **2**, **4**—**6**, *i.e.*, when passing from **1** to **7**, **2** to **7**, **4** to **9** (or **4** to **10**), **5** to **10**, and **6** to **9**, the LUMO energy becomes less negative in all cases, *i.e.*, the LUMOs are destabilized. The replacement of X = F by X = Cl also increases the LUMO energy (see Table 2). This means that the mechanism of π_3^*-stabilization occurs due to the fluorine atom (see Fig. 3). Thus, the inductive effect of the halogen can be considered to be the principal factor that determines the low reduction potential of the compounds under study.

It should be expected from the calculated LUMO energies that compounds **7**—**10** should be oxidized at more negative potentials, while acetylenes **11** and **12**, the products of two-electron reductive elimination should be oxidized at much more negative potentials. However, in most cases, we observed only one wave or peak of reduction of the starting reagents, corresponding to 1—1.5 V. The second wave of the reduction was sometimes observed only for substances **3** and **6** at potentials −2.0 and −1.70 V, which corresponds to the from 1 to 1.5 electrons.

In our view, a feasible explanation for the results obtained in this study (if, perhaps, not the single explanation) is the following. Reduction is followed by dimerization of the anion radicals with the subsequent elimination of two halide ions (see Scheme 3, sequence 1—3). Then, the one-electron reduction of substituted butadienes to sufficiently stable anion radicals occurs at the same potentials:

$$\text{RCF=CFX} + \text{e} \rightleftharpoons (\text{RCF=CFX})^{\cdot -}$$

$$(\text{RCF=CFX})^{\cdot -} \longrightarrow 1/2\ \text{R}\overset{\ominus}{\text{C}}\text{F—CFX—CFX—}\overset{\ominus}{\text{C}}\text{FR}$$

17

$$1/2\ \mathbf{17} \xrightarrow{\text{fast}} 1/2\ \text{RCF=CF—CF=CFR} + 2\,\text{X}^{\ominus}$$

$$1/2\ \text{RCF=CF—CF=CFR} + 1/2\ \text{e} \rightleftharpoons (1/2\ \text{RCF=CF—CF=CFR})^{\cdot -}$$

One and a half electrons are consumed per substrate molecule in the total reaction, which is in agreement with our experimental data. The inverse peak of the oxidation of the butadiene anion radical can be shifted more than 60 mV farther to the anodic side than the cathode substrate peak. The ratio of the height of the anode peak to that of the cathode peak should not be more than 0.5/1.5 = 0.33, which is close to our experimental results.

It is possible to explain the absence of anodic peaks at the Pt electrode and their presence at the Hg and GC electrodes in the framework of the proposed reaction scheme. As is known,[22] the reduction of difficultly reduced RX organic halides at the electrode can sometimes be easily done with the aid of mediators called electron transfer reagents; various one-electron reducible organic compounds, yielding a stable reversible $A/A^{\cdot -}$ redox pair, can, in particular, serve as mediators. The necessary condition is that the formation potential of the $A^{\cdot -}$ anion radical has to be less negative than the substrate reduction potential. The anion radical of mediator $A^{\cdot -}$ formed on the electrode (Eq. (1)) serves as the initiator of the process of mediator reduction; the anion radical donates its electron to the substrate molecule (Eq. (2)).

$$A + e \xrightleftharpoons{\text{cathode}} A^{\cdot -} \quad (1)$$

$$A^{\cdot -} + RX \longrightarrow A + RX^{\cdot -} \quad (2)$$

$$RX^{\cdot -} \longrightarrow R^{\cdot} + X^{-} \quad (3)$$

$$R^{\cdot} + A^{\cdot -} \longrightarrow A + R^{-} \quad (4)$$

The initially reversible process of mediator reduction becomes irreversible in the presence of the substrate, since the anion radical of the mediator is consumed according to Eqs. (2) and (4), whereas the current of mediator reduction increases (the formation of the nonreduced form of the mediator occurs (see also Eqs. (2) and (4))). The higher the concentration of the substrate with respect to the concentration of the mediator, the more the reduction current of the latter increases, and the reversibility of mediator reduction is lost to a greater degree. In this case the efficiency of the reduction of the substrate by the mediator is strongly dependent on the difference of their potentials $\Delta E = E^0{}_{A/A^{\cdot -}} - E_{RX}^{Red}$. This value should not be too high, since this will hinder the electron-transfer process; it also should not to be too low since, in that case, a parallel reduction of the substrate at the electrode will occur and a portion of the mediator molecules will not participate in the electron donation process. It is possible that the diene $(RCF{=}CF{-}CF{=}CFR)^{\cdot -}$ anion radicals formed at the electrode during the reduction of RCF=CFX alkenes can participate in the reduction of starting compounds as mediators. If the potential scanning into the anodic region is performed after the reduction of RCF=CFX, the electron transfer from the anion radical to the substrate should occur in the potential interval where the $(RCF{=}CF{-}CF{=}CFR)^{\cdot -}$ anion radical and the unreduced form of the starting alkene exist simultaneously. Therefore, the anodic peak of reoxidation of the anion radical in question will not be recorded on the Pt electrode, which is just the case:

$$RCF{=}CFX + (RCF{=}CF{-}CF{=}CFR)^{\cdot -} \rightleftharpoons (RCF{=}CFX)^{\cdot -} + RCF{=}CF{-}CF{=}CFR$$

The anodic peaks that appear during the reduction of RCF=CFX at the GC and Hg cathodes can be explained by the fact that the E^{Red} potentials of the compounds under study at these electrodes are more positive than those at the Pt electrode, whereas the E^0 potential of the reversible butadiene RCF=CF—CF=CFR/$(RCF{=}CF{-}CF{=}CFR)^{\cdot -}$ pair must not depend on the electrode material. This means that the difference of potentials $\Delta E = E^0{}_{(RCF=CF-)_2/RCF-)_2^{\cdot -}} - E^{Red}{}_{RCF=CFX}$ can be so small that the interval of potentials where the butadiene radical and unreduced substrate form exist simultaneously on the GC and Hg electrodes will be narrower than that on the Pt electrode. In principle, this is tantamount to a decrease in the concentration of substrate relative to mediator, as compared to the case considered for the Pt electrode. Thus, when using GC and Hg electrodes, not all $(RCF{=}CF{-}CF{=}CFR)^{\cdot -}$ anion radicals participate in the mediator reduction of alkene, but some of their portion is reoxidized at the electrode to yield the observed anodic peaks. The assumption of the possible reduction of the RCF=CFX alkenes with the aid of $(RCF{=}CF{-}CF{=}CFR)^{\cdot -}$ anion radicals is confirmed, in particular, by the fact that the alkene reduction current increases as the number of potential scans in the forward and backward directions increases. This effect is most pronounced at the Pt electrode.

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