Russian Chemical Bulletin, International Edition, Vol. 50, No. 11, pp. 1929—1935, November, 2001 1929

Electrochemical activation of freons using electron transfer mediators

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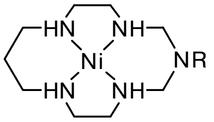
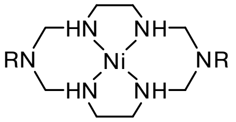
This overview discusses the electrochemical activation of freons $CF_2ClCFCl_2$ (CFC113), CF_3Br (FC13B1), and CF_2Cl_2 (CFC12) using various electron transfer mediators: complex nickel(II) compounds with nitrogen-containing tetradentate ligands and bipyridyl, aromatic derivatives (perylene, *p*-dicyanobenzene, *E*-azobenzene, and others), and sulfur dioxide. A possibility was shown of the homogeneous catalytic activation of freons by two mutually supplementing electron transfer mediators: methylviologen—SO_2 and I_2—SO_2. The involvement of freons by the electron transfer mediators into the syntheses of valuable organic products under mild conditions was demonstrated for several examples.

Key words: activation of freons, electrocatalysis, homogeneous catalysis of transformation of freons, conversion of freons into valuable organic products, trifluorochloroethylene, fluoroalkylaryl sulfides, azamacrocyclic nickel(II) complexes.

In recent years, the problem of activation of freons attracts attention. This is associated with the known problems of decomposition of the ozone layer and a search for ways of the alternative use of current large-scale (tens millions of tons)[1] manufacturing of freons. One of these ways can be the application of freons in syntheses of valuable organic products. In particular, freons can serve[2] as convenient sources of the fluoroalkyl groups in the electrosynthesis of various fluoro-containing organic compounds (fluorinated carboxylic and sulfonic acids, ethers and thio ethers, and others), the raw materials for the electrochemical preparation of fluoroethylenes, which are widely used in the synthesis of fluoroplastics, *etc.* However, the direct electrochemical reduction (ER) of freons, especially chloro-containing, requires considerable energy expenses because it is performed at high negative potentials. In this respect, their indirect ER using electron carriers (mediators) from a cathode to freon can be a more attractive approach. To present time, this ER of freons is poorly studied. CF_3Br is virtually the only studied[2—4] object of this class of compounds, whereas many works are devoted to the electrocatalytic activation of nonfluorinated aryl and alkyl halides.


$[NiL^1]^{2+}$: R = H
$[NiL^2]^{2+}$: R = Me
$[NiL^3]^{2+}$: R = CH_2CH_2OH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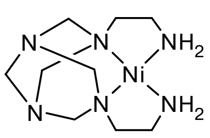
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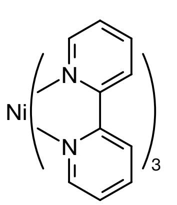
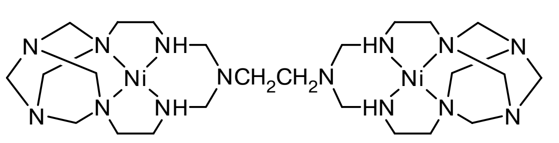

$Ni(bipy)_3^{2+}$


$[Ni_2L^6]^{4+}$

In this review, we present the results of our studies of the electrochemical and homogeneous catalytic activation of freons $CF_2ClCFCl_2$ (CFC113), CF_3Br (FC13B1), and CF_2Cl_2 (CFC12) with various electron mediators (metal complexes, aromatic molecules, radical ions, *etc.*) and exemplify the use of the mediator—freon systems in the synthesis of valuable organic products.*

We studied the activation of ER of the above freons by nickel(II) complexes with the nitrogen-containing tetradentate ligands ($[NiL^n]^{2+}$ (n = 1—5) and $[Ni_2L^6]^{4+}$) and bipyridyl ($Ni(bipy)_3^{2+}$) as mediators.[5]

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* All experiments were carried out in a solution of DMF, which was purified by double vacuum distillation and drying with molecular sieves 4A, using of 0.1 *M* Bu_4NBF_4 as a base electrolyte purified by recrystallization from an ethyl acetate—hexane mixture. Voltammetric studies were carried out at 25 °C in a three-electrode cell with the platinum disk working (d = 0.5 mm) and counter electrodes and an Ag/AgCl reference electrode. For recording CVA curves, a setup based on an ER-20A potentiostat and PC was used. The latter allowed the study in a wide sweep range (0.01—100 V s^{-1}). Preparative electrolysis was performed in a cell divided with a glass filter (Pt cathode, Zn anode) in the potentiostatic or amperostatic regime (a PI-50-1 potentiostat). The reaction products were identified by the elemental analysis, mass spectrometry, ^{19}F NMR, IR spectroscopy, argentometry, and other methods. Procedures for the study and isolation of the reaction products are described in detail in our works cited here.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1843—1849, November, 2001.
1066-5285/01/5011-1929 $25.00 © 2001 Plenum Publishing Corporation

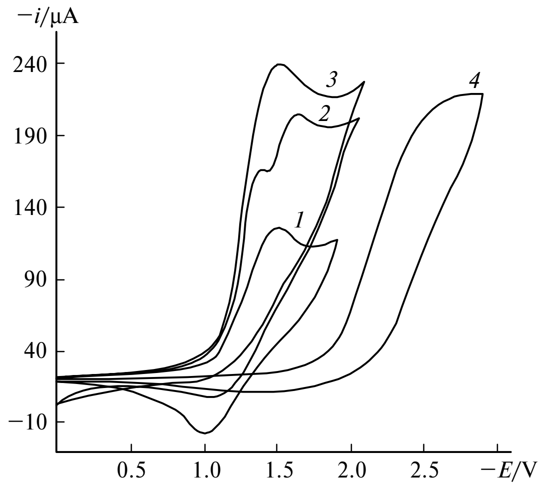


Fig. 1. Cyclic voltammograms of $[\mathrm{NiL}^1]^{2+}$ in the absence (*1*) and presence of freon CFC113 at freon to complex ratios of 0.25 : 1 (*2*) and 0.5 : 1 (*3*) and individual CFC113 (*4*); DMF, 0.1 *M* $\mathrm{Bu_4NBF_4}$, $v = 0.1$ V s^{-1}.

Perchlorates of the cations $[\mathrm{NiL}^n]^{2+}$ (n = 1—5), $[\mathrm{Ni_2L^6}]^{4+}$, and $\mathrm{Ni(bipy)_3}^{2+}$ were synthesized according to procedures described previously.**[6,7]**

Two one-electron cathodic peaks are observed in the CVA curves for the $[\mathrm{NiL}^n]^{2+}$ (n = 1—5) and $[\mathrm{Ni_2L^6}]^{4+}$ complexes. The first of them corresponds to the quasi-reversible one-electron $\mathrm{Ni^{II}/Ni^{I}}$ transition at potentials (E_c^1) in the −1.45 to −1.65 V region (Fig. 1, Table 1). The electronic structure of the R substituents in the $[\mathrm{NiL}^n]^{2+}$ (n = 1—4) complexes has no noticeable effect on the E_c^1 values (see Table 1) because the methylene groups are poor transmitters of the electron effect of these substituents. The region of higher negative potentials contains the second irreversible ER peak corresponding to the $\mathrm{Ni^{I}/Ni^{0}}$ transition (E_c^2, see Table 1). Unlike nickel azamacrocyclic complexes, the CVA curve for $[\mathrm{Ni(bipy)_3}]^{2+}$, under the experimental conditions, exhibits two one-electron quasi-reversible peaks, first of which (see Table 1) corresponds to $\mathrm{Ni^{II}/Ni^{I}}$ transition. This suggests that bipyridyl ligands have somewhat higher stabilizing effect on the lowest oxidation state of the metal than the tetradentate ligands.

Table 1. Potentials of cathodic (E_c^1, E_c^2) and anodic (E_a^1) peaks in CVA curves for the studied complexes and the ratio of the catalytic (i_kp) to diffusion (i_dp) currents at the E_c^1 potentials in the presence of a tenfold excess of CFC113

Complex	$-E_\mathrm{c}^1$	$-E_\mathrm{c}^2$	$-E_\mathrm{a}^1$	$i_\mathrm{kp}/i_\mathrm{dp}$
		V		
$[\mathrm{NiL}^1]^{2+}$	1.65	1.08	2.13	3.4
$[\mathrm{NiL}^2]^{2+}$	1.60	1.26	2.06	3.2
$[\mathrm{NiL}^3]^{2+}$	1.58	1.25	2.09	3.6
$[\mathrm{NiL}^4]^{2+}$	1.61	1.14	2.13	4.2
$[\mathrm{NiL}^5]^{2+}$	1.47	1.17	1.95	3.3
$[\mathrm{Ni_2L^6}]^{4+}$	1.50	1.03	—*	2.0
$\mathrm{Ni(bipy)_3}^{2+}$	1.17	1.03	1.89**	1.0

* In the potential region lower than −2.75 V the peak is absent.
** The anodic peak at $E_\mathrm{a}^2 = -1.74$ V is also observed.

Under the indicated conditions, CFC113 is reduced irreversibly and at much higher negative potentials ($E < -1.8$ V, see Fig. 1) than the reduction of $\mathrm{Ni^{II}}$ to $\mathrm{Ni^{I}}$ in the studied macrocyclic and bipyridyl complexes.

The addition of minor amounts of freon to a DMF solution of the $[\mathrm{NiL}^n]^{2+}$ complexes (n = 1—4) changes the shape of the CVA curves in the region of the $\mathrm{Ni^{II}/Ni^{I}}$ transition. For example, in the case of $[\mathrm{NiL}^1]^{2+}$ (see Fig. 1, curve *2*), the anodic peak disappears, and a new cathodic peak ($E_\mathrm{c}^{1\prime}$) appears at more negative potentials. As the freon concentration increases and the ratio of the freon to complex concentrations achieves 0.5 : 1, the current of two cathodic peaks increases, and they run into each other (see Fig. 1, curve *3*). Similar changes are also observed in the CVA curves for $[\mathrm{NiL}^5]^{2+}$, $[\mathrm{Ni_2L^6}]^{4+}$, and $[\mathrm{Ni(bipy)_3}]^{2+}$ (Fig. 2) when freon CFC113 is added to their solutions. However, in this case, the cathodic peaks are well resolved and characterized by a substantial shift of potentials to a more negative region with an increase in the freon concentration.

Changes in the shape of voltammograms similar to above discussed have previously been formed for the ER of the $\mathrm{Ni^{II}}$ complexes in the presence of various halogen-containing compounds, in particular, 2-chloro- and 2-bromobut-2-ene,**[8]** chloro- and bromobenzene,**[9—11]** and iodobenzene.**[12]** Taking into account the results of these studies, we can propose a general scheme for the ER of freons ($\mathrm{R_fHal}$) catalyzed by $[\mathrm{NiL}^n]^{2+}$ (n = 1—5) and $[\mathrm{Ni_2L^6}]^{4+}$ complexes. The key stages in this scheme (Scheme 1) are the ER of the starting $\mathrm{Ni^{II}}$ complex (**1**) to a $\mathrm{Ni^{I}}$ compound, the formation of the intermediate nickel—substrate complex (**2**), and its subsequent ER.

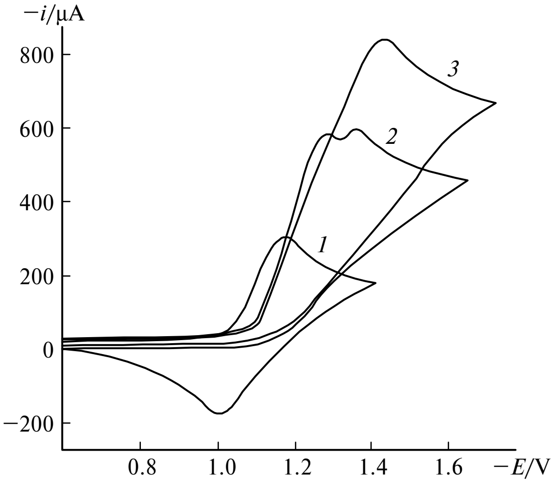
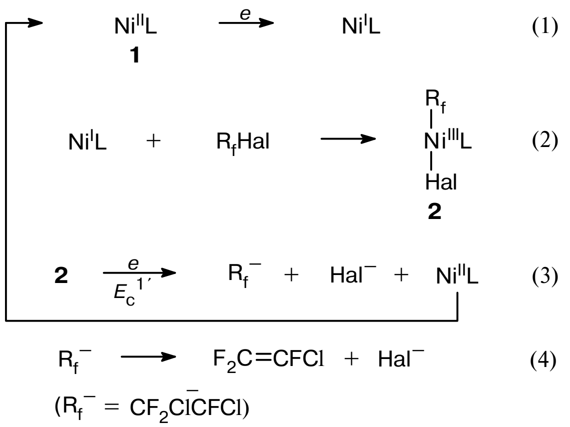


Fig. 2. Cyclic voltammograms of $\mathrm{Ni(bipy)_3}^{2+}$ in the absence (*1*) and presence of freon CFC113 at freon to complex ratios of 0.5 : 1 (*2*) and 1 : 1 (*3*); DMF, 0.1 *M* $\mathrm{Bu_4NBF_4}$, $v = 0.1$ V s^{-1}.

Scheme 1



Probably, this is precisely the last stage, which is related to the appearance of the new peak ($E_c^{1'}$) in the CVA curve of complex **1** in the presence of freon. The simultaneous regeneration of complex **1** results in the appearance of the catalytic component of the current. The R_f^- anion is formed at the same stage as the third reduction product. When freon CFC113 is reduced, this anion can decompose to eliminate the halide anion and generate trifluorochloroethylene (TFE), which is a valuable initial compound for the synthesis of fluoroplastics, anesthetics, and others.

The ability of these nickel complexes to efficiently catalyze the ER of freon CFC113 to form TFE according to Scheme 1 has been confirmed by the results of preparative studies.**5** For example, when using $[Ni(bipy)_3]^{2+}$ as a mediator, freon CFC113 can be reduced at a potential ($E = -1.2$ V) much less negative than that ($E = -3.2$ V, *vs.* SCE) at which CFC113 was directly reduced.**13** Moreover, in the presence of this complex, CFC113 is converted**5** to TFE in almost 100% yield. The electrolysis products do not contain fluoro-derivatives of ethane or butane, which could be expected in the case of participation of fluoroalkyl radicals as intermediates formed during the transfer of the halogen atom or an electron.**14**

The character of changes in the CVA curves for the nickel complexes with the addition of CFC113 to a solution can be determined, according to Scheme 1, by the ER potentials of complexes **1** and **2**, regeneration rate of the initial complex **1**, which depends on the stability of intermediate **2**, and the rate of Ni^{II}/Ni^{I} ER. Note some qualitative regularities of such changes with an increase in the concentration of CFC113. Already at a ratio of the freon to complex concentrations of 0.5 : 1 (in the case of $[NiL^n]^{2+}$, where $n = 1-4$) we observe only one reduction peak for complexes **1** and **2**, and its intensity increases with an increase in the freon concentration as it takes place, *e.g.*, for $[NiL^1]^{2+}$ (see Fig. 1, curve *3*). This fact indicates, most likely, the relative stability of intermediate **2** and a comparatively high rate of its formation. In addition, for the considered complexes, unlike $[Ni(bipy)_3]^{2+}$ (see Fig. 2), an increase in the freon concentration does not result in such a substantial shift of the peak potential to the cathodic region. This indicates a very high rate of the reactions composing the catalytic cycle.

The shape of the CVA curves for $[NiL^5]^{2+}$, $[Ni_2L^6]^{4+}$, and $[Ni(bipy)_3]^{2+}$ in the presence of CFC113 changes in somewhat different manner. In the case of $[Ni(bipy)_3]^{2+}$, at a ratio of the freon to complex concentrations of 0.5 : 1, the CVA curve exhibits reduction peaks for both complexes **1** and **2** (see Scheme 1, Fig. 2, curve *2*), and the potentials and current values of the peaks slightly differ. An increase in the CFC113 concentration results in running of two peaks into one and the shift to the cathodic region of potentials (see Fig. 2, curve *3*). This can be related to an increase in the contribution of the catalytic current component. We found that the character of transformation of the CVA curves in the case of $[NiL^5]^{2+}$ or its binuclear analog $[Ni_2L^6]^{4+}$ is close to that described above.

Since it is difficult, in some cases, to distinguish the peaks of complexes **1** and **2** in the ER of freon CFC113, the efficiency of the above catalytic effect of the mediators can be estimated from the ratio of the catalytic (kinetic) current (i_{kp}) to the diffusion current (i_{dp}) observed at high CFC113 concentrations (when peaks of complexes **1** and **2** run into each other). The data obtained for a tenfold excess of CFC113 over the mediator are presented in Table 1. It follows from their analysis that the efficiency of the catalytic effect of the studied complexes (i_{kp}/i_{dp}) increases with the shift of the potential of their reduction to the cathodic region. This is related to a decrease in the energy gap ΔE between the reduction potentials of the complex and freon and the facilitation of electron transfer from the reduced form of the mediator to the freon molecule (see Scheme 1, step (1)). The highest i_{kp}/i_{dp} ratios are observed for $[NiL^1]^{2+}$, $[NiL^3]^{2+}$, and $[NiL^4]^{2+}$, which are characterized, most likely, by higher rates of catalytic reactions.

The reduction potential of the mediator is an important but not single feature determining the efficiency of the catalytic effect of the complexes. This is why, most likely, the i_{kp}/i_{dp} and E_c^1 values are not related by a linear dependence. For example, the difference in the electrochemical behavior of the $[NiL^n]^{2+}$ complexes at $n = 1-4$, on the one hand, and $[NiL^5]^{2+}$, $[Ni_2L^6]^{4+}$, on the other hand, in the presence of freon CFC113 can be related to differences in their spatial structure. In the case of $[NiL^n]^{2+}$ ($n = 1-4$), the equatorial ligands do not create steric hindrances for the axial nickel—substrate interaction to form structure **2** (see Scheme 1). At the same time, the presence of the tetraazabicyclononane fragment in the $[NiL^5]^{2+}$ and $[Ni_2L^6]^{4+}$ complexes can result in the steric repulsion between the ligands that form the inner coordination sphere in complex **2**. This effect should result in a weakening of the $Ni-R_f$ bond and, hence, influence the kinetic parameters of the catalytic processes.

We found[5] that the studied nickel complexes can be used as efficient mediators for the ER of CFC113 and other freons. In particular, changes in the CVA curves of $[Ni(bipy)_3]^{2+}$ similar to those found in the presence of CFC113 also take place when freons FC13B1 and CFC12 are added to a solution; however, the potentials of the reduction peaks of complexes **1** and **2** at comparable concentrations of fluoroalkyl halides somewhat differ. For example, for FC13B1 the potentials of the reduction peak of intermediate **2** are shifted by 0.08 V to the region of less negative potentials compared to that of a similar peak of CFC113. This can be related to higher electron-withdrawing properties of the trifluoromethyl group in the organonickel complex.

We studied a possibility for the ER of freon CFC113 using not only nickel azamacrocyclic and bipyridyl complexes but also various aromatic outer-sphere electron carriers: *p*-dicyanobenzene, *p*-diacetylbenzene, fluoranthene, perylene, and *E*-azobenzene.[15]

Compared to freon CFC113, the electroreduction of these compounds occur, under the same conditions, at less negative potentials ($E° = -1.3$ to -1.7 V) (Table 2) and is reversible. This is indicated, in particular, by the equality of the currents of the cathodic and anodic peaks (Fig. 3, curve *1*). When adding freon to a solution of the mediator, the cathodic current increases and the anodic current decreases in the CVA curve of the mediator, and the current of the cathodic peak increases linearly with an increase in the concentration of the added freon (see Fig. 3, curves *2* and *3*). The obtained results agree with the general mechanistic scheme (Scheme 2) for the ER of substrates (RX) bearing the potentially leaving group (X) by outer-sphere electron transfer mediators (Med).[16] This general scheme coincides mainly with Scheme 1. They differ by a possibility of the formation of complex **2** at the stage of homogeneous electron transfer (see Scheme 1, step (2)) followed by its reduction at $E_c{}^{1\prime}$.

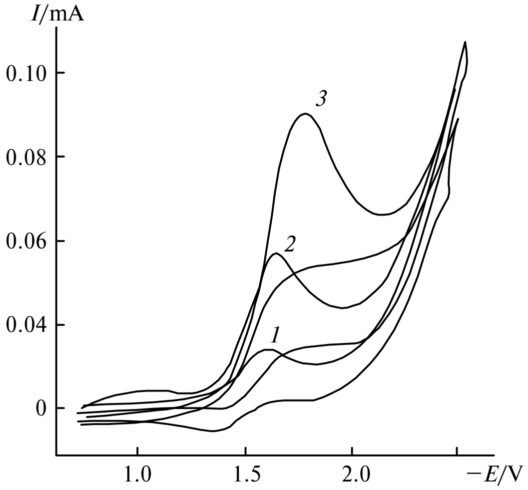


Fig. 3. Cyclic voltammograms of the electrochemical reduction of dicyanobenzene (10^{-2} mol L^{-1}) in the presence of freon CFC113 at freon to mediator ratios of 0 : 1 (*1*), 2 : 1 (*2*), 5 : 1 (*3*); DMF, 0.1 *M* Bu_4NBF_4, $v = 0.1$ V s^{-1}.

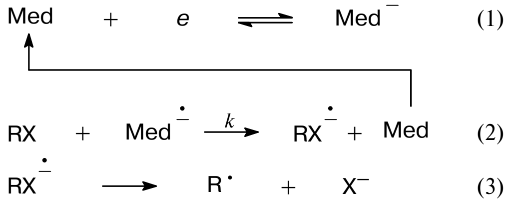
Table 2. Catalytic effects (i_k/i_d) and rate constants of electron transfer from the mediator radical anion to freon (*k*) *vs.* standard redox potential of the mediator (*E*°)

Mediator	−*E*°/V	i_k/i_d*			$k^{**} \cdot 10^{-3}$ /L mol^{-1} s^{-1}
		A	*B*	*C*	
E-Azobenzene	1.28	1.2	1.2	1.1	4.1
p-Diacetylbenzene	1.40	1.9	1.7	1.4	17.4
p-Dicyanobenzene	1.48	3.0	2.4	1.8	82.1
Perylene	1.56	3.4	3.2	2.4	127
Fluoranthene	1.68	3.6	3.2	2.6	841

* The i_k/i_d values were measured at freon to mediator ratios of 2 : 1 and sweep rates of 5 (*A*), 10 (*B*), and 50 V s^{-1} (*C*).

** Accuracy of determination ±10%.

Scheme 2



We determined the values of catalytic effects (i_k/i_d) for the studied mediators during the activation of the ER of freon CFC113 in a wide range of sweep rates (Table 2 exemplifies the i_k/i_d ratios for three sweep rates and Table 3 contains those for different freon concentrations). As can be seen from these data, the catalytic effect depends substantially on the redox properties of the mediator and increases with the shift of its standard redox potential to the negative region on going from azobenzene to fluoranthene. This regularity is observed at all sweep rates used.

A more universal characteristics of the catalytic activity of a mediator, compared to the catalytic effect, is

Table 3. Catalytic effects (i_k/i_d) for the freon 113—*p*-dicyanobenzene system at different sweep rates (*v*)

v/V s^{-1}	i_k/i_d*		
	A	*B*	*C*
0.2	2.0	3.1	7.0
10.0	1.6	2.4	3.9
50.0	1.4	1.8	2.9

* The i_k/i_d values were measured at freon to mediator ratios of 1 : 1 (*A*), 2 : 1 (*B*), and 5 : 1 (*C*).

the rate constant of the interaction of its active form (radical anion) with a substrate. A comparison of the experimental and theoretically calculated voltammograms was used[15] for the calculation of the rate constants (k) (see Table 2) of electron transfer from the mediator radical anion to freon (see Scheme 2, step (2)). We developed an approach that allows the comparison of experimental and theoretical voltammograms corresponding to different sweep rates along the whole CVA curve, which increases the accuracy of determination of the kinetic parameters compared to those obtained by the known methods[16—18] using only the dependence of the catalytic effect on the sweep rate.

As follows from the data in Table 2, the calculated k values increase substantially (more than 200-fold) on going from azobenzene to fluoranthene. The redox potential of the mediator shifts to the negative region, and the difference of the reduction potentials (ΔE) of freon and mediator decreases. At the same time, analysis of the obtained results shows a linear correlation (Fig. 4) between logarithms of rate constants and standard redox potentials of the mediators ($\ln k = -13.18E^\circ - 8.55$, $r = 0.99$), confirming an assumption about the outer-sphere character of the electron transfer in the mediator—freon system. This correlation makes it possible to predict the rate constant of the electron transfer from the mediator radical anion to the freon molecule, *i.e.*, the catalytic efficiency of the mediator in this process, from the redox potential of the outer-sphere mediator of the considered type.

Preparative studies for the freon CFC113—*p*-dicyanobenzene pair were carried out[15] to reveal the nature of products formed in the activation of the ER of freon CFC113 by the indicated organic mediators. It is known[13] that the direct electrochemical dechlorination of freon CFC113 in the hexametapol—water mixture at $E = -3.2$ V (*vs.* SCE) results in the formation of TFE (8% yield) and 1,1,2-trifluoro-1,2-dichloroethane (3%). We succeeded in a more efficient electrochemical conversion of freon CFC113 to TFE

$$F_2ClC{-}CFCl_2 \xrightarrow[-2Cl^-]{+2e,\ Med} F_2C{=}CFCl$$

at $E = -1.4$ V in 85% yield of TFE per substance and 65% per current due to the use of the mediator.[15]

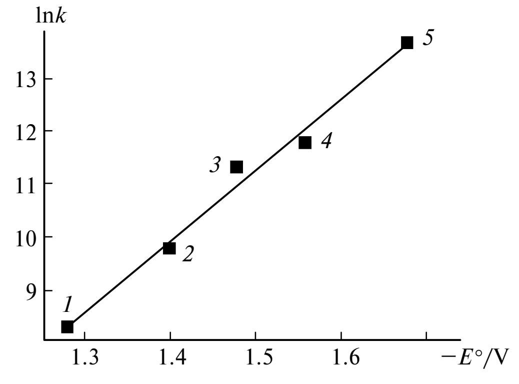


Fig. 4. Plot of the logarithm of the rate constant of the electron transfer from the mediator radical anion to freon (ln*k*) *vs.* standard redox potential of the mediator (*E*°): *E*-azobenzene (*1*), *p*-diacetylbenzene (*2*), *p*-dicyanobenzene (*3*), perylene (*4*), and fluoranthene (*5*).

Along with the above metal complex and aromatic mediators, some simpler compounds capable of undergoing reversible redox transformations, for example, SO_2, can act as electron mediators during the ER of freons.[19—21] As shown previously,[21] in the case of freon FC13B1 (CF_3Br), the electron transfer rate from the $SO_2^{\cdot-}$ radical anion to CF_3Br by four orders of magnitude exceeds that for outer-sphere organic mediators. This process was assumed[21] to occur *via* the inner-sphere mechanism with the simultaneous elimination of the Br^- ion and can occur in the solvent cage.

$$CF_3Br + SO_2^{\cdot-} \longrightarrow CF_3^{\cdot} + SO_2Br^-$$
$$(\rightleftharpoons SO_2 + Br^-)$$

The fluoroalkyl radicals generated in this process can react, at subsequent stags, with the $SO_2^{\cdot-}$ radical anion or with SO_2 to form fluoroalkyl sulfinates, whose current yield reaches[21,22] 60—90% depending on the conditions.

It was of interest to reveal a possibility of using this electrochemical system for the utilization of freons and synthesis of other valuable compounds, for example, perfluoroalkylaryl sulfides, which are widely used for the preparation of insecticides, sensitizers, biologically active substances, *etc.* CF_3I is usually used[23—25] as a trifluoromethylating agent for the synthesis of trifluoromethyl sulfides from thiophenols, and thiophenols can readily be trifluoromethylated in high yields electrochemically[19,26] using the cathodic activation of CF_3I. At the same time, the use of much more accessible and cheap reagent, CF_3Br, either results in a much lower yield of the target products or requires more drastic conditions. Its electrochemical activation is carried out at higher negative potentials. The latter can be related to several factors, one of which is a high probability of the fast ER of the $CF_3^{\cdot}$ radicals, formed in the one-electron ER of CF_3Br, to carbanions directly on a cathode (the $CF_3^{\cdot}$ radicals are more easily reduced than the starting freon[3,27]). This prevents a sufficiently high concentration of the $CF_3^{\cdot}$ radicals in a solution, which is necessary for the efficient preparation of trifluoromethylaryl sulfides. The introduction of the electron transfer mediator from the cathode to CF_3Br into the reaction medium would allow, on one hand, the activation of CF_3Br at lower potentials and, on the other hand, would favor the transition of the activation process from the near-electrode layer into the solution. We found[28] that this effect really took place. The use of SO_2 as an electron mediator allows the fluoroalkylation of thio-

Table 4. Yield of trifluoromethylaryl sulfides *p*-$XC_6H_4SCF_3$ upon the electrocatalytic trifluoromethylation of the corresponding thiophenols with freon FC13B1 in the presence of SO_2 as mediator

X	Yield (%)	
	per substance	per current
$NHCOOCH_3$	94	376
H	78	312
Br	64	252
Cl	60	240
NO_2	24	96

phenols in very high yields per substance (Table 4). As follows from the data in Table 4, the yields of trifluoromethylaryl sulfides per current, except for *p*-nitrotrifluoromethylphenyl sulfide, much exceed 100%, indicating the occurrence of an energy-saving chain radical process in which the current is consumed for its initiation only (Scheme 3).

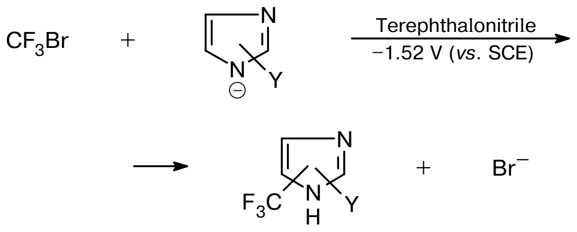
Scheme 3

$$SO_2 + e \rightarrow SO_2^{-\cdot} \qquad (1)$$
$$SO_2^{-\cdot} + CF_3Br \rightarrow SO_2 + CF_3^{\cdot} + Br^- \qquad (2)$$
$$CF_3^{\cdot} + SO_2^{-\cdot} \rightarrow CF_3SO_2^- \qquad (3)$$
$$CF_3^{\cdot} + SO_2 + e \rightarrow CF_3SO_2^- \qquad (4)$$
$$CF_3^{\cdot} + XC_6H_4S^- \rightarrow [XC_6H_4SCF_3]^{-\cdot} \qquad (5)$$
$$[XC_6H_4SCF_3]^{-\cdot} + SO_2 \rightarrow XC_6H_4SCF_3 + SO_2^{-\cdot} \qquad (6)$$

The high yields of the trifluoromethylation products of thiophenols (see Table 4) indicate that in the studied systems the route of the interaction of $CF_3^{\cdot}$ with the thiophenolate ions is predominant of three possible competing processes of binding trifluoromethyl radicals (see Scheme 3, reactions (3)—(5)).

Using such an outer-sphere mediator as terephthalonitrile, we can involve**[4,29]** freon CF_3Br into the electrochemical trifluoromethylation of styrene, benzimidazoles, and imidazoles (Scheme 4).

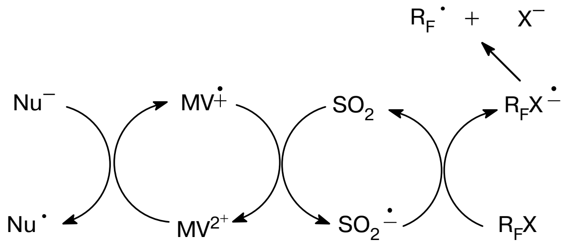
Scheme 4



We have previously found**[25]** that the reactions of perfluoroalkyl iodides with nucleophiles, in particular, with thiophenols, resulting in the formation of perfluoroalkylaryl sulfides in the absence of the electric current, can be catalyzed by methylviologen (MV^{2+}). At the same time, the use in such syntheses of much cheaper freons, *e.g.*, CF_3Br, as fluoroalkylating agents instead of fluoroalkyl iodides seems impossible because MV^{2+} cannot transfer an electron from thiophenol to less active CF_3Br. In turn, as it is shown above, SO_2 can serve as an efficient electron mediator from the cathode to CF_3Br.

Taking into account both these factors, we proposed and substantiated the double mediatory MV^{2+}—SO_2 system, which can perform cascade electron transfer from the nucleophile to freons, activate the latter under mild conditions, and involve them in fluoroalkylation reactions of, *e.g.*, thiophenols, with a high yield of the target products (R_F—Nu)**[30]** (Scheme 5). The homogeneous catalytic I_2—SO_2 system of two supplementary mediators can perform the same efficient electron transfer from the nucleophile to freon.**[31]**

Scheme 5



Thus, our studies showed that freons can be activated under mild conditions and involved in the synthesis of valuable organic products using inner-sphere and outer-sphere electron mediators. Taking into account the significance of the problem of a search for nontraditional routes of using freons, we can expect an intensification of works in this are in the nearest future.

This article was written on the basis of results obtained by the authors in cooperation with V. E. Titov, L. A. Kiprianova, L. I. Fileleeva, K. G. Tsanov, P. B. Paramonov, and others.

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Received February 7, 2001;
in revised form June 19, 2001