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Electrochemical Reduction of Nitrogen-Fluorine Bonds: Relevance to the Reactivity of Electrophilic Fluorinating Agents

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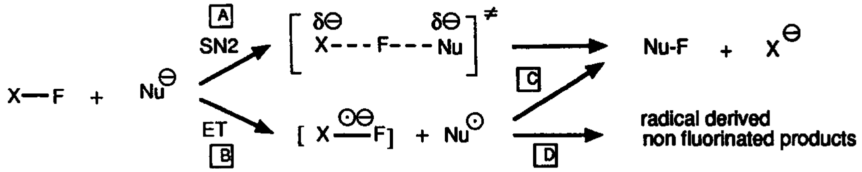
Key words: Fluorination; polarography; voltammetry; reduction; electron transfer.

Abstract: The cyclovoltammetric and polarographic behaviour of nitrogen-fluorine bond containing compounds, including representative electrophilic fluorinating agents is described. The reduction potentials are strongly affected by the substituents on the nitrogen atom and by the electrode material. All reductions are irreversible on the investigated time scale. The influence of these results on the reactivity of electrophilic fluorinating agents is discussed.

Electrophilic fluorinating agents[1] containing nitrogen-fluorine bonds have become extremely useful tools to introduce fluorine into organic compounds.[2-12] Although widely used in organic synthesis, these reagents have remained poorly understood with respect to the mechanism of the fluorine transfer step (scheme 1).[13,14]



Scheme 1: Possible pathways in the reaction of Nu$^{\ominus}$ with X-F

The high enthalpy of formation of the cation F$^{\oplus}$ in the gas phase (420 kcal/mol) as well as the identification of radical derived products or intermediates have been taken as arguments for a two-step pathway where an electron transfer (ET) precedes a fluorine radical transfer (route B-C). Nucleophilic attack at fluorine via an S_N2 pathway (route A) has mostly been considered as unlikely. Thus an electron transfer is proposed as the first step in fluorinations with N-fluoro-perfluoropiperidine[15] as well as with N-fluoro-pyridinium salts.[16] Based on electron transfer theory, we have, however, shown recently that an S_N2 at fluorine is the only pathway which can account for the observed products and rate constants in the reactions of the saccharin derived N-fluoro-sultam with a variety of nucleophiles.[17,18] Electron transfer (ET) appears to be a competing reaction which does not lead to fluorinated products (route D). Since this competition between S_N2 and ET is influenced by the redox potentials of the reaction partners, ET theory should be a powerful tool to rationalize or predict the chemical behaviour of electrophilic fluorinating agents as it allows to calculate under what conditions ET can occur.[19,20] This, however, requires a better knowledge of the electrochemical behaviour of such reagents. Few data on nitrogen-fluorine compounds are available in the literature. According to Ward, HNF_2 is reduced in acetonitrile at -1.42 V (vs. SCE) in a $4e^{\ominus}$ process.[21] H_2NF, the intermediate formed, is reduced at a potential no more cathodic ($E_{1/2} \geq -1.42$ V vs. SCE), since ammonia is the final product of the reaction. The half-wave potential of HNF_2 shifts to -1.23 V in aqueous media, slightly less negative than for NF_3, which is reduced at -1.40 V (vs. SCE).[22] The reduction of alkyl substituted difluoramino compounds occurs in aprotic media in the potential range from -1.10 to -1.60 V (vs. SCE). No details are given concerning the structure of the alkyl part.[23] N-fluoro- and N-fluoro-N-methyl urethane are reduced at -1.81 and -1.75 V (vs. SCE), respectively.[24] Perfluorinated amidine or guanidine derivatives are reduced in acetonitrile at -0.2 V (vs. SCE).[25] In all cases, the reduction appears to be an irreversible process.

This paper reports voltammetric and polarographic results of selected N-fluoro-derivatives, including recently published fluorinating agents. Peak potentials (E_p) measured at the stationary glassy carbon electrode and half-wave potentials ($E_{1/2}$), measured at the dropping mercury electrode (DME) are summarized in tables. The electrochemical behaviour of N-fluoro-sultam[7,8] derivatives and N-fluoro-benzenesulfonimide[11] is outlined and the influence of the nitrogen substituents on the reduction potential is discussed.

Table 1 summarizes the behaviour of N-fluoro-sultams and N-fluoro-benzenesulfonimide - recently published as electrophilic fluorinating agents[7,8,11] - in comparison to the electrochemical behaviour of the parent N-H compounds. N-fluoro-sultam <u>1</u> is reduced on a stationary glassy carbon electrode in acetonitrile/0.1 M nBu_4NClO_4 in a single well-formed broad wave (E_p= -1.21 V, vs. SCE) at scan rates from 10 to 200 mV s^{-1}. A typical cyclic voltammogramm at a scan rate of 200 mV s^{-1} is shown in Figure 1. Peak height and peak potential exhibit a good reproducibility. On repetitive cycling no blocking of the electrode surface appears. Between the peak height (i_p) and the depolarizer concentration (c) a fair linearity is observed in the studied range (Figure 2). The pattern of the voltammogram (no peak on return of the potential and wave width (E_p-$E_{p/2}$)) and [α.n] (α= charge transfer coefficient; n = number of electrons transferred) of 0.250 (derived from Galus equation: $E_{1/4} - E_{3/4} = 0.052/\alpha n$)[26] with n=2 indicate a strongly irreversible reduction process. The logarithmic analysis of the reduction step of the N-fluoro-sultam <u>1</u> yields a slope of 95 mV. Addition of water or of a weak acid (HOAc) had no significant effect on the height of the step. A brief investigation of the cyclovoltammetric behaviour of the N-fluoro-sultam at a stationary Au, Pt, Au(Ag) electrode and the hanging mercury drop electrode (HMDE) shows a complex behaviour with a strong shift of the E_p towards less negative potentials as a function of the electrode material.[27] This suggests that organometallics might be involved as intermediates in the electroreduction of N-F compounds. Organomercurials have been proposed as intermediates in the reduction of N-X compounds:[24,28]

$$RCONRX + Hg^o \text{--->} RCONRHgX$$

$$RCONRHgX + 2e^- \text{--->} RCONR^- + Hg^o + X^-$$

A double wave is found at the HMDE. No or only a small, ill-developed wave, merging with the rest current is observed for Pt and Au, when measured under the conditions of the glassy carbon electrode. Since the parent sultam <u>2</u> is not reduced in the analyzed potential range, we attribute this irreversible step to the reductive cleavage of the N-F bond. The nitro-substituted sultam <u>3</u> gives multiple reduction waves due to the additional electrochemically active nitroaryl group with a first wave located at E_p= -0.79 V (vs. SCE). Since the parent sultam <u>4</u> is reduced at a potential only slightly more negative (E_p= -0.97 V, vs. SCE), this first wave probably corresponds to an electron transfer from the electrode to the doubly activated aromatic ring. The camphor derived N-fluoro-sultam 5 is reduced at -1.58 V, the parent compound 6 giving no wave in the analyzed range of potentials. N-fluoro-benzenesulfonimide 7 is reduced at -0.54 V, thus showing the strong influence of a second sulfonyl group on the reduction potential of N-fluoro-sulfonamide derivatives. The parent sulfonimide is reduced at -1.49 V, which compares well with literature values for arylsulfonamides.[29] As for 1, less negative reduction potentials are observed for the N-fluoro-derivatives 3, 5 and 7 at the mercury electrode. A complex behaviour is found for 5, indicating possible follow-up reactions at the electrode.

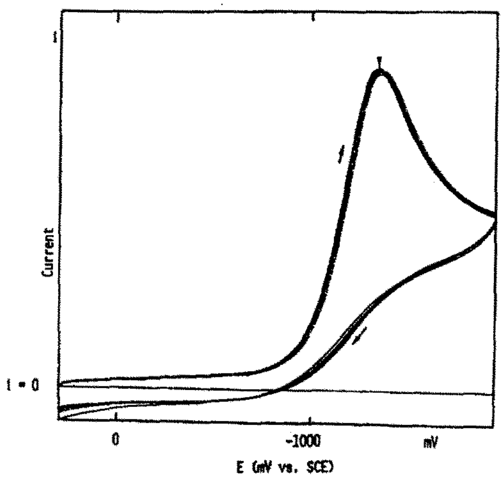


Figure 1: Cyclovoltammograms (10 repetitive runs) of N-fluorosultam 1, measured at a stationary glassy carbon disk electrode (3 mm); supporting electrolyte: 0.1 M tetrabutylammonium perchlorate/acetonitrile; scan rate = 200 mV s^{-1}; N-fluorosultam concentration = 1.1×10^{-3} M; temperature = 23∓0.5°C

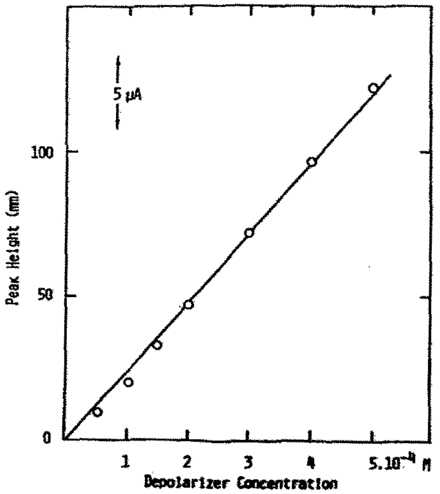
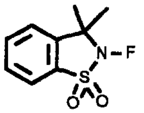
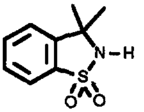
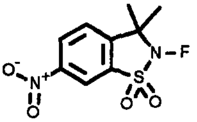
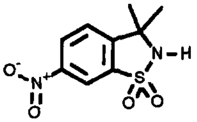
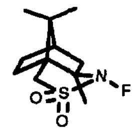
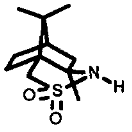
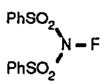
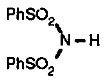


Figure 2: Peak height (i_p) as a function of the N-fluorosultam concentration; scan rate = 200 mV s^{-1}.

Table 1: Electrochemical reduction of sultam and sulfonimide derivatives:

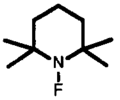
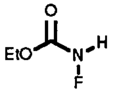
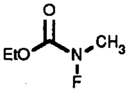
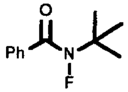
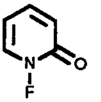
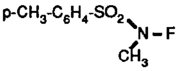
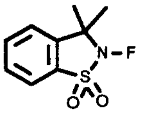
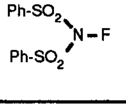
Compound	E_p (V, vs. SCE)	$E_{1/2}$ (V, vs. SCE)
 1	-1.21	-0.31
 2	no wave	no wave
 3	-0.79	-0.23
 4	-0.97	-0.97
 5	-1.58	-0.53[a] -0.86[a] -1.26[a]
 6	no wave	no wave
 $(PhSO_2)_2N-F$ 7	-0.54	+0.16
 $(PhSO_2)_2N-H$ 8	-1.49	-1.56

a. very large merged waves

Table 2 shows the influence of the nitrogen substituent on the reduction of the N-F bond. On glassy carbon E_p values for the monoactivated N-F amides and sulfonamides 1,13-15 lie between -1.21 and -1.53 V (vs. SCE). Compounds 14 and 15 have been described as fluorinating agents by Purrington[4] and Barnette.[3] With two sulfonyl groups (7), the E_p shifts to a considerably less negative value (-0.54 V), as shown above.

The unactivated N-fluoro-tetramethylpiperidine 10, in contrast, gives no reduction wave in the measured range of potentials. No E_p values have been reported for 9, 11 and 12. As can be seen, all potentials measured at a mercury electrode lie at considerably less negative or for 7 even at a positive value (vs. SCE). The unactivated compound 10 is reduced under these conditions, although the wave occurs at a very negative potential, similar to that reported for N-fluoro-urethane derivatives.

Table 2: Influence of the activating group:

Compound		E_p (V, vs. SCE)	$E_{1/2}$ (V, vs. SCE)
H_2NF	9	n.m.[a]	-1.42[21]
	10	no wave	-1.77
	11	n.m.[a]	-1.81[24]
	12	n.m.[a]	-1.75[24]
	13	-1.53	-1.48
	14	-1.52	-1.30
 $p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2N(CH_3)\text{-}F$	15	-1.44	-0.50
	1	-1.21	-0.31
 $(Ph\text{-}SO_2)_2N\text{-}F$	7	-0.54	+0.16

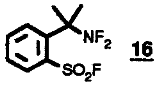
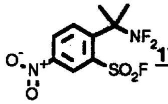
a. n.m. = not measured in the cited work.

Since none of the corresponding parent nonfluorinated compounds is electrochemically active in the applied potential range (NH_3, secondary amines, urethanes, amides, sulfonamides and 2-pyridone are not active at the potentials analyzed here;[30] for compounds 2 and 8, see Table 1), we attribute the observed wave to the reduction of the N-F group. On both electrodes, there is a steady shift of the peak potential to less negative values in the order alkyl ≈ urethane < amide ≈ lactam < sulfonamide ≈ sultam < sulfonimide.

This trend correlates well with the electron withdrawing power of the substituents, although the values for 9 and 10 are somewhat less negative than expected. For 9 this could be the result of solvent effects, since it has been shown that the reduction potential of this compound strongly depends on the solvent and its water content.

The introduction of additional fluorine atoms on the nitrogen has relatively little influence on the reduction potentials (Table 3). With the exception of 17, where the first wave can again be attributed to the nitro substituted aromatic ring, all RNF_2 and NF_3 are reduced at potentials between -1.1 and -1.6 V vs. SCE on mercury.

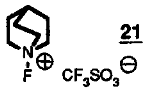
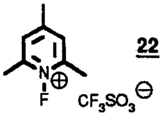
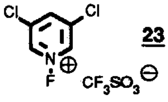
Table 3: Electrochemical reduction of NF_2 compounds and NF_3:

Compound	E_p (V, vs. SCE)	$E_{1/2}$ (V, vs. SCE)
 16	-1.65	-1.62
 17	-0.82	-0.80
HNF_2 18	n.m.[a]	-1.42[21]
$AlkNF_2$ 19	n.m.[a]	-(1.1-1.6)[23]
NF_3 20	n.m.[a]	-1.42[22]

a. n.m. = not measured in the cited work

Positively charged N-F derivatives are reduced at low negative potentials on glassy carbon and even at positive potentials (21 and 23) on mercury (Table 4).

Table 4: Electrochemical reduction of $N^{\oplus}$-F compounds

Compound	E_p (V, vs. SCE)	$E_{1/2}$ (V, vs. SCE)
 21	-0.63	+0.085
 22	-0.65	-0.21
 23	-0.10	+0.32

N-fluoro-quinuclidinium triflate, introduced by Banks,[5b] is reduced at E_p= -0.63 V (vs. SCE). Since tetraalkylammonium salts are not reduced in the indicated potential range, the observed peak can be attributed to the reduction of the N-F bond. The reduction of N-fluoro-pyridinium salts, published as fluorinating agents by Umemoto[10] and based on initial results of Meinert[16] strongly depends on the substituents of the pyridine ring, the 3,5-dichloro derivative beeing reduced at -0.10 V, in comparison to N-fluoro-collidinium triflate, reduced at -0.65 V. Since N-alkyl-pyridinium salts are reduced reversibly to the corresponding radical at potentials ranging from 0 to -1.0 V, depending on the substituents,[30,31] the reduction of N-fluoro-pyridinium salts might be a more complex process involving either ET to the N-F bond, or, alternatively, to the π-system of the aromatic ring. We take, however, the irreversibility of the reduction step as well as the strong shift to less negative values on the mercury electrode - which we take as an indication that fluorine is involved in the reduction step - as a hint that the reduction wave corresponds to the reductive cleavage of the N-F bond.

The following conclusions can be drawn from these results:

1. The reduction potential of compounds containing nitrogen-fluorine bonds is strongly affected by the substituents of the nitrogen atom. In the series studied, shifts of the measured reduction potentials of the N-F bond of about 2 V are observed, which represents a difference of the standard free energy change associated with the electron transfer of more than 45 kcal mol^{-1} !

2. Nitrogen-fluorine bond containing compounds activated by electron-withdrawing substituents or those in which fluorine is attached to a positively charged nitrogen atom possess a fairly high oxidizing power and it should not be surprising to see ET reactions with a variety of nucleophiles.

3. All electrochemical reductions appear to be irreversible on the chosen time scale. We attribute this to the reductive cleavage of the nitrogen-fluorine bond with loss of the fluoride anion. A more detailed investigation of the mechanism of this cleavage is in progress.[32] An important consequence of this reductive cleavage is that the potentials measured at the inert glassy carbon electrode reflect - in analogy to the reduction of alkyl halides[33] - a considerable overpotential in comparison to "reversible" potentials which will have to be used to calculate electron transfer rates using ET theory. We have confirmed this previously by calculating an E° value which accounts for the ET reaction between 1 and tetramethyl phenylene diammine (E°= -0.67 V vs. SCE in contrast to a measured E_p= -1.21 V vs. SCE).[18] Therefore, the measured reduction potentials should represent a lower (i.e. most negative) limit of the E° which has to be used in the calculation of electron transfer rates.

4. These figures should allow an estimation of potential exothermal electron transfer steps and thus a rationalization of redox reactions observed with electrophilic fluorinating agents containing N-F bonds.

To summarize, this work represents the first extensive comparison of the electrochemical behaviour of nitrogen-fluorine containing compounds. Together with literature data on reduction potentials of other fluorinating agents, this should contribute to rationalize the reactivity of electrophilic fluorinating in general.[34]

Experimental part:

1. General.

All chemicals used for electrochemical measurements were of analytical grade and were used without further purification. The N-F compounds used in this study were prepared as described or in analogy to literature procedures. N-fluoro-sulfonamide 15 and the N-fluoro-pyridinium derivatives 22 and 23 are commercially available. The difluoramino derivatives 16 and 17 are obtained as side products in the fluorination of the corresponding sultams with elemental fluorine. The syntheses of new compounds are described below. Fluorinations with elemental fluorine were run in an ambient pressure reactor as described by Auer et al.[35] ^{1}H-NMR and ^{19}F-NMR spectra were measured on a Bruker WM 250 or a Varian XL 300 with TMS, resp. $CFCl_3$, as internal standards.

N-fluoro-7-nitro-saccharinsultam 3

Through a solution of 10 g (20 mmol) of m-nitro-saccharinsultam 4 in 300 ml CH_3CN at -45°C is passed a stream of F_2/N_2 (10% w/w) for 1 h (60 mmol). After evaporation of the solvent and chromatography on silica gel, 5.3 g (50%) of N-fluoro-m-nitro-saccharinsultam 3 are obtained. ^1H-NMR (ppm, $CDCl_3$): 1.78 (d, J=5 Hz, 6 H), 7.6 (d, J=8 Hz), 8.5 (dd, J=8 Hz, 1.5 Hz), 8.6 (d, j=1.5 Hz); ^{19}F (ppm, $CDCl_3$): -41.82

7-nitro-saccharinsultam 4

20 g (0.1 mol) of saccharinsultam are dissolved in 75 ml concentrated H_2SO_4. Then a mixture of 10.3 ml (0.22 mol) HNO_3 and 11.9 ml (0.22 mol) H_2SO_4 is added dropwise. After a slightly exothermal reaction (40°C) the yellow solution is stirred at room temperature for 26 h. CH_2Cl_2 is added and the phases are separated. The organic phase is washed with saturated aqueous sodium bicarbonate, dried and concentrated to give 26.2 g (90%) of N-nitro-7-nitro-saccharinsultam. Treatment with 400 ml H_2SO_4 at 70°C for 26 h, neutralization with NaOH and extraction with CH_2Cl_2 gives 20.2 g (92%) of m-nitro-saccharinsultam 4. ^1H-NMR (ppm, CD_3CN): 1.73 (s, 6 H), 4.96 (broad s, 1 H), 7.6 (d, J=8 Hz, 1 H), 8.5 (dd, J=8 Hz, 2 H), 8.6 (d, J=2 Hz).

N-fluoro-2,2,6,6-tetramethyl piperidine 10

4.23 g (30 mmol) of 2,2,4,4-tetramethylpiperidine in 50 ml diethyl ether are cooled to -78°C, then 18.75 ml (30 mmol) n-BuLi (1.6 M in hexane) are added dropwise. The resulting solution is stirred at -78°C for 1 h, diluted with 50 ml diethyl ether and 9.45 g (30 mmol) of N-fluoro-benzenesulfonimid are added in small portions. The suspension is stirred for 1 h at -78°C, then warmed up to room temperature. After quenching with a saturated solution of aqueous ammonium chloride, extraction with diethyl ether and drying over sodium sulfate, the solvent is distilled off at normal pressure to give 1.3 g (28%) of 10 as a light brown liquid. ^1H-NMR (ppm, $CDCl_3$): 1.25 (broad singlet), 1.60 (broad singlet); ^{19}F-NMR (ppm, $CDCl_3$): -96.97 (lit.[36]: -96.0).

N-fluoro-N-t-butyl benzamide 13

0.7 g (4 mmol) of N-t-butyl benzamide are added in small portions to 0.176 g (4.4 mmol) of KH in diethyl ether. After stirring at room temperature for 1 h, the suspension is diluted with 5 ml THF, then 1.64 g (5.2 mmol) of N-fluoro-benzenesulfonimide are added in small portions. Stirring at room temperature for 1 h and then at 30-40°C for 1 h gives a yellow solution. Quenching with 0.1 N HCl and extraction with CH_2Cl_2 followed by chromatography over silica gel gives 75 mg (10%) of 13. ^1H-NMR (ppm, $CDCl_3$): 1.45 (d, J= 2 Hz , 9 H), 7.3-7.5 (m, 4 H), 7.64 (m, 1 H); ^{19}F-NMR (ppm, $CDCl_3$): -65.27.

2-(1-methyl-1-difluoramino)-ethyl-benzenesulfonyl fluoride 16

16 is obtained as a secondary product by overfluorination of 2 in presence of NaF ^1H-NMR (ppm, $CDCl_3$): 1.8 (broad s, 6 H), 7.5 (m, 1 H), 7.7 (m, 2 H), 8.23 (d, J=8 Hz, 1 H); ^{19}F-NMR (ppm, $CDCl_3$): 27.1 (NF_2), 64.1 (SO_2F).

2-(1-methyl-1-difluoramino)-ethyl-5-nitro-benzenesulfonyl fluoride 17

Through a solution of 5 g (20.6 mmol) of m-nitrosultam 4 and 10 g of finely powdered dry NaF in acetonitrile is passed a stream of F_2/N_2 (10% w/w) for 1.5 h (90 mmol). The precipitate is filtered off and the solution is concentrated. Purification by chromatography on silica gel gives 3.4 g (63%) of 17. ^1H-NMR (ppm,$CDCl_3$): 1.95 (broad s, 6 H), 8.13 (d, J=8 Hz, 1 H), 8.64 (dd, J=8 Hz, 2 Hz, 1 H), 9.07 (d, J=2 Hz, 1 H); ^{19}F-NMR (ppm, $CDCl_3$): 27.5 (NF_2), 64.4 (SO_2F).

2. Electrochemical techniques.

2.1. Apparatus

An Amel Model 471 multipolarograph was used in conjunction with a three-electrode 10 ml thermostated polarographic cell. Working electrode: for cyclo voltammetric measurements a stationary glassy carbon disk electrode (diameter 3 mm, Metrohm 6.0804.010) was used. The stationary Pt disc electrode was obtained from Beckmann, the Au disk electrode from Metrohm. All solid electrodes were - if not mentioned otherwise - carefully polished with Al_2O_3 (0.5 μm), rinsed with doubly distilled water and supporting electrolyte before each new measurement. The hanging mercury drop electrode (HMDE) was of the Belami-type. A saturated calomel electrode (SCE) was used as reference electrode. It was connected to the cell solution by means of a double salt-agar bridge containing supporting electrolyte. The auxiliary electrode was a platinum wire.

2.2. Procedure

The experiments were carried out in a mixture of 0.1 M tetrabutylammonium perchlorate/ acetonitrile as supporting electrolyte. All solutions were deoxygenated with supporting electrolyte saturated oxygen-free nitrogen for ≥ 10 min before measurement. The measurements were performed at controlled temperature (23 ∓ 0.5°C). Cyclic voltammetric measurements used to characterize the electrochemical behaviour of the various compounds studied, were run under identical conditions with following instrument settings:

Scan = 100 mV s^{-1}; initial potential = +100 mV (vs. SCE); start of the scan in negative direction; potential range examined = from +100 to -2500 mV (v. SCE). Settings for compounds **7**, **23** : $E_{initial}$ = +400 mV (vs. SCE); potential range examined from +400 to -2500 mV (vs. SCE). Concentration of the individual compounds (depolarizers) studied = 1.10^{-3} M. The cyclovoltammogram of N-fluoro-7-nitro-saccharinsultam **3** served for the calibration of the measured potentials within different experimental series.

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References and notes:

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