

Variation of the electrochemical transfer coefficient in the electroreduction of aromatic two-ring disulfonyl difluorides

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An attempt has been made to describe quantitatively the variation of transfer coefficient with potential in the electroreduction of twelve aromatic two-ring disulfonyl fluorides of $\text{FO}_2\text{S-Ar-M-Ar-SO}_2\text{F}$ type, where -M- is a bridging group. Each compound exhibits two two-electron steps of $-\text{SO}_2\text{F}$ reduction. Linear relationship exists between α and the potential, E . The average value of $\partial\alpha/\partial E$ is 0.42 V^{-1} . The limiting values of potential corresponding to $\alpha = 1$ and $\alpha = 0$ are calculated and discussed. The series of compounds covers ca. 40% of the total range of α variability.

The variation of the electrochemical transfer coefficient with potential has been an important subject of electrochemical interest for over three decades. Recent reports suggest that the transfer coefficient, α , does change with potential (cf. reference 1 and references cited therein) in the way predicted by the modern theories of charge transfer²⁻⁴.

This work deals with the investigation of variation in transfer coefficient not within the potential range of a single compound, but for a series of related compounds, with the aim of covering, possibly, the widest range of potentials. Hence, the variation of α from compound to compound is considered. Furthermore, the presence of two reactive groups in one molecule makes it possible to follow the changes in α while two successive groups in a single compound are being reduced. The problem of α variation within a single functional group has been investigated earlier¹ and it is not considered here.

Variation of transfer coefficient for a different series of substituted compounds with the same reactive group has already been discussed⁵. The significance and utility of the transfer coefficient values for some organic compounds was the subject of another paper⁶.

Materials and Methods

The compounds listed in Table 1 were prepared specially for this work. No published data on any of them were found in literature. All were prepared by the known reaction between potassium fluoride and the respective sulfonyl chloride^{7,8}. (The data on the latter can be found in

ref. 9). Mass spectra of the compounds confirmed their calculated molecular weights.

The measurement system was a three-electrode one and was used in conjunction with an XY-4105 recorder and an EP20A potentiostat. The capillary yield in a circuit open to air was $1.090 \times 10^{-3} \text{ g/s}$. It was siliconated using the procedure described in literature¹⁰. The measurements were made at $298 \pm 0.05 \text{ K}$. Solutions of sulfonyl fluorides ($1.3 \times 10^{-3} \text{ M}$) in 0.1 M methanolic $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ were used. The reference electrode was SCE containing LiCl solution in methanol. Platinum electrode served as the auxiliary electrode. The two electrodes were separated from the sample solution with a transition vessel with glass sinter.

All current-potential curves were recorded point by point in 0.005 V steps; the constant drop time was 2.00 s . The number of electron exchanged was determined in the standard way by using diaphragm electrolyser. The catholyte volume was 100 cm^3 and depolarizer mass: $3 \times 10^{-4} \text{ mol}$.

Results

The reduction

Each of the twelve compounds studied in this work reacted in such a way that one could distinguish steps of reduction of individual SO_2F groups, although for most of them a detailed examination was required (Table 2). Compound 8, for example, yielded two well separated waves, each related to reduction of one SO_2F group. The second wave partially overlapped a third one.

Table 1—Aromatic disulfonyl difluorides used in the present study*

Number	Compound	Melting point, °C
1		249-250
2		183-184.5
3		122-123
4		126.5-127.5
5		111-112
6		138.5-141.5
7		144-144.5
8		120-122
9		201.5-202.5
10		246.5-247.5
11		277-279
12		246-247

*All compounds were purified by repeated crystallization from chloroform. Compound 6 was additionally purified by sublimation.

This third wave remained unchanged after full hydrolysis of the compound as revealed by a separate experiment and hence it was attributed to the reduction of carbonyl group. This wave was of no significance to the main results.

Compound 7 yielded two nearly fully separated reduction waves of SO_2F groups and a separate third wave at a more negative potential. Only this third wave remained after complete hydrolysis of the compound.

Compounds 1 and 2 each yielded one (unsplit) wave attributable to reduction of both $-\text{SO}_2\text{F}$ groups and another one at much more negative potentials. Only the last one remained after complete hydrolysis of the compounds.

Compounds 3-6 and 9-11 produced single waves due to SO_2F reduction; for compounds 9-11, however, the waves nearly split (inflexion could be seen on current vs. potential curves).

For compound 12, a single wave was observed in the potential range -0.4 to -0.6 V, which was ascribed to reduction of $-\text{N}=\text{N}-$ bridge. Another wave appeared in the range -1.55 to -1.85 V corresponding to reduction of both the SO_2F groups. After hydrolysis, only the first wave remained, with its potential range and limiting current being very similar to those in the original compound 12.

It was found coulometrically that each wave corresponding to the reduction of SO_2F group was a two-electron wave, or in the case of overlapping waves, a four-electron one. Respective sulfinic acids were the products of reduction.

The separated two-electron waves were dealt with in the standard way; the values $(E_{1/2})_1$, $(an)_{\text{obs},1}$ and $(E_{1/2})_2$, $(an)_{\text{obs},2}$ were determined for each SO_2F group. The values of k_h were calculated from Tafelian segments^{11,12} of polarographic waves using the typical relationship,

$$i = nFAk_h c_{\text{ox}} \quad \dots (1)$$

where c_{ox} is the reagent concentration (mol/cm^3), A is the electrode surface (cm^2), i is the current (A), and

$$k_h = k_{h,0} \exp[anF(E - E_0)/RT] \quad \dots (2)$$

with $k_{h,0}$ being k_h at the potential assumed to be zero.

Evaluation of the individual values of $(E_{1/2})_1$, $(an)_1$, $(E_{1/2})_2$, $(an)_2$ from the complex four-electron waves required selection of several representative points on the curve in the whole range of the complex wave, calculation of the currents (i_{calcd}) at respective potentials, and their comparison with the experimental values of currents, i_{exp} . The analysis was carried out until all calculated currents fell onto the experimental i vs. E curve with the lowest error. The least squares method was used for this. The results are presented in Table 2.

Table 2 contains the products $(an)_{\text{obs},T}$ for four compounds from the series of sulfonyl fluorides evaluated in Tafelian regions of i vs. E curves. $\bar{E}$ denotes the potential in the middle of Tafelian region. The values were determined only for the compounds with separated waves or for those at least exhibiting well pronounced limiting current inflexion in i vs. E curve.

Table 2 — Electroreduction of disulfonyl difluorides in 0.1 *M* methanolic $N(C_2H_5)_4I$. Values of halfwave potentials, $E_{1/2}$, and the products $(\alpha n)_{obs}$ and $(\alpha n)_{obs,T}$ determined from Tafelian relations; $\bar{E}$ denotes the middle of Tafelian segment

No.	$(E_{1/2})_1$, $(E_{1/2})_2$, [V]	$(\alpha n)_{obs,1}$ $(\alpha n)_{obs,2}$	Standard devn, [%]	$\bar{E}$, [V]	$(\alpha n)_{obs,T,1}$ $(\alpha n)_{obs,T,2}$
1	-0.949 -1.011	1.05 0.96	1.9		
2	-1.048 -1.110	1.14 1.13	2.0		
3	-1.183 -1.318	0.91 0.76	2.0	-1.099 —	0.95 —
4	-1.443 -1.495	0.84 0.64	3.5		
5	-1.496 -1.615	0.76 0.58	2.6		
6	-1.515 -1.589	0.76 0.64	3.5	-0.788 —	1.25 —
7	-0.828 -0.966	1.37 1.35	1.2	-0.788 —	1.25 —
8	-1.025 -1.362	1.16 0.84	—	-0.960 -1.275	1.08 0.79
9	-1.134 -1.280	1.01 0.92	1.8	-1.059 —	0.96 —
10	-1.126 -1.307	0.95 0.82	1.5	-1.058 —	0.91 —
11	-1.416 -1.558	0.87 0.76	2.3	-1.360 —	0.74 —
12	-1.645 -1.730	0.78 0.62	2.2		

The parameters that characterize reduction processes (for each wave under consideration) are: (i) electrochemical order with respect to substrate: 1 ± 0.1 ; (ii) reaction order with respect to $N(C_2H_5)_4^+$: 0.85 ± 0.1 ; and (iii) reaction constant $\rho_\pi(\rho) > 0$ (slope of the relation $E_{1/2}$ vs. σ or $\log k_h$ vs. σ).

Discussion

The plots of $(\alpha n)_{obs}$ vs. $E_{1/2}$ and of $(\alpha n)_{obs,T}$ vs. $\bar{E}$ drawn by using data from Table 2 were both found to be linear. The relevant equations are:

$$(\alpha n)_{obs} = (1.892 \pm 0.208) + (0.7637 \pm 0.1572) E_{1/2} \quad \dots (3)$$

$$(n = 24 \text{ points}; r = 0.9066)$$

and

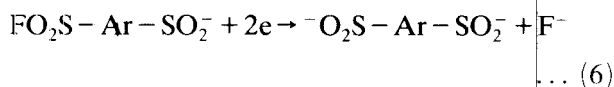
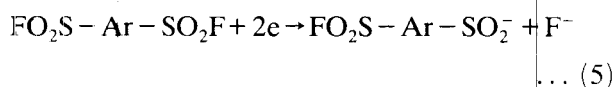
$$(\alpha n)_{obs,T} = (1.918 \pm 0.230) + (0.8874 \pm 0.2091) \bar{E} \quad \dots (4)$$

$$(n = 7 \text{ points}, r = 0.9796).$$

The second equation describes reduction of SO_2F groups in the compounds with separated waves or with at least clear inflexion in the limit-

ing current line on the first wave. Hence, it is related to the reduction of one SO_2F group. The Tafelian relationships refer to the initial region of wave formation. Therefore, for the parameters to have physical significance for the first reduced group, the reduction current for the second wave has to be negligibly small. Calculations confirmed it to be true in each case. This is why Eq. (4) covers the compounds with sufficiently different $(E_{1/2})_1$ and $(E_{1/2})_2$ values.

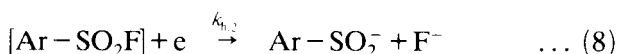
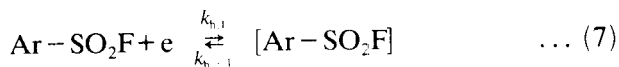
An interpretation of the relationships presented in Figs 1 and 2 becomes possible after discussing the mechanism of reduction in detail. The results suggest the following stepwise mechanism of electroreduction of SO_2F groups.



The values of $(\alpha n)_{\text{obs}}$ presented in Table 2 are related to a two-electron electroreduction of SO_2F group and hence they must be complex quantities. It is known that electroreduction of SO_2X group (where X is a halogen) is an irreversible process that does not split into two one-electron steps in both protic and aprotic media^{13,14}. Disproportionation of the anion-radical resulting from addition of the first electron can probably be excluded;

otherwise, a part of the substrate would have formed inactive $\text{Ar}-\text{SO}_3^-$ anion and the measured number of electron exchanged would have fallen below $2F/\text{mol}$ of SO_2F . The actual experimental value is 2 ± 0.05 , or 4 ± 0.1 for the two overlapping waves. Furthermore, the radicals containing sulfur are rather inactive¹⁵. Further electroreduction of anion radical seems, therefore, justified.

All this reasoning together with experimental findings discussed above including the high (αn) values suggest the following mechanism of reduction:



The mechanism represented by Eqs 7-8 is of IIB type according to Alberly's classification of multistep processes¹⁶ with the observed rate constant,

$$k_{h,\text{obs}} = \frac{k_{h,1} k_{h,2}}{k_{h,-1}} \quad \dots (9)$$

This IIB case (with $k_{h,-1} > k_{h,2}$) is more sensitive to potential (two electrons in transition state) than IIA where $k_{h,1}$ value controls the total rate of the process. Hence, using Eq. (9) and the definition of transition coefficient, we can write

$$\alpha_{\text{obs}} = \alpha_1 + \alpha_2 - \alpha_{-1} \quad \dots (10)$$

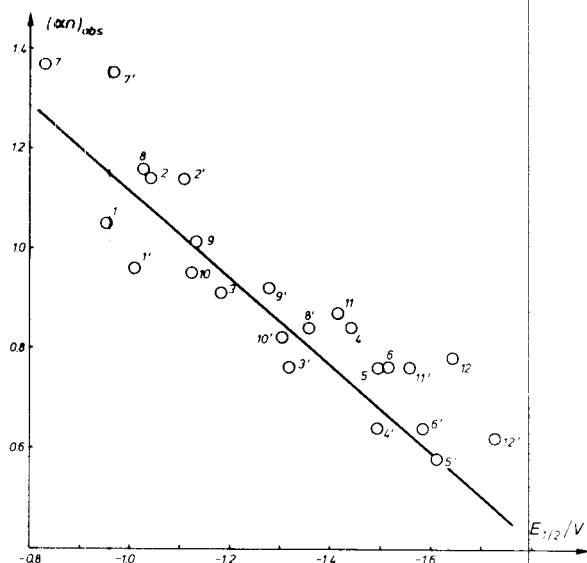


Fig. 1—Electroreduction of a series of disulfonyl difluorides in 0.1 M methanolic $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$. The plot shows relationship between $(\alpha n)_{\text{obs}}$ and half wave potentials determined using the equation describing irreversible waves.

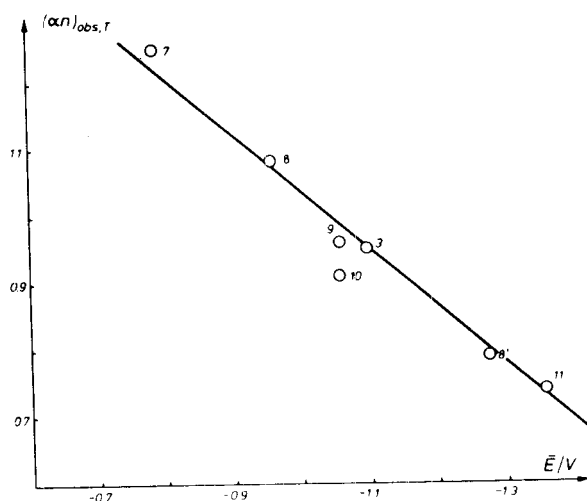


Fig. 2—Electroreduction of a series of disulfonyl difluorides in 0.1 M methanolic $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$. The plot of $(\alpha n)_{\text{obs,T}}$ determined from Tafelian relations, vs. $\bar{E}$, the potential in the middle of Tafelian segments.

A relation similar to (10) can be deduced by using Eq. (1) for the currents: $i = i_1 + i_2$, where i_1 and i_2 are the currents for one-electron steps. Thus,

$$(\alpha n)_{\text{obs}} = \alpha_1 + \alpha_2 \quad \dots (11)$$

Equations (10) and (11) reveal the origin of the complex (αn) values and make it possible to discuss their variations.

Of particular interest are the limiting values of potential obtained by extrapolation of $(\alpha n)_{\text{obs}}$ and $(\alpha n)_{\text{obs},T}$ [Eqs (1) and (2)] to the limits 0 and 2. The limiting value of 2 should be replaced by the value of $\alpha_1 = 1$ if one considers Eq. (10) with $\alpha_{-1} = 0$ (oxidation process) or $\alpha_1 = 1$ directly by Eq. (11). The average limiting values are $E = -2.35 \pm 0.15$ V $\{(\alpha n)_{\text{obs}} = \alpha_{\text{obs}} = 2\alpha_1 = 0\}$ and $E = 0.12 \pm 0.02$ V $\{(\alpha n)_{\text{obs}} = \alpha_{\text{obs}} = 2\alpha_1 = 2\}$ respectively.

The significance of $E = -2.35$ is that starting from that value potential does not affect the electroreduction process any more and the rate is controlled by addition of electron to the substrate in the so called activationless process¹⁷. According to the polarization theory of metal-electrolyte interface¹⁸, desorption of the so called surface hydrated electron takes place with the formation of free hydrated electron. The limiting potential is also close to the potential of decomposition of supporting electrolyte ($\approx 2.2 \pm 0.1$ V for 0.1 M $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ in methanol). According to Antropov¹⁹, such a decomposition is accompanied by emission of hydrated electron to solution.

The other limiting value of 0.12 V, close to zero in hydrogen scale, determines the range of the maximum effect of the potential upon electroreduction process where the rate is controlled solely by subtraction of electron from electrode. From the theoretical point of view, this corresponds to the so called barrierless process¹⁷.

The limiting values of α and corresponding potentials resulting from Eqs (3) and (4) are consistent with those predicted by the theory.

A similar discussion of the limiting values of transfer coefficients might be carried out referring to the close analogy between the equations of electrochemical kinetics and Brønsted equation. Here, it seems important that the experimental lowest and highest αn values: 0.58 and 1.37, respectively (Table 2), or $\alpha_1 = 0.29$ and 0.69, correspond to the intermediate region of Brønsted linear relation and cover ca. 40% of the total range of variability of the elementary transfer, or Brønsted coefficient.

The average slope of the plot of $(\alpha n)_{\text{obs}}$ vs. pot-

ential, $d(\alpha n)_{\text{obs}}/dE$, is 0.42 V^{-1} and this magnitude is consistent with values both predicted theoretically and measured experimentally (cf. refs. 20 & 21). Quite unexpectedly, values very close to the same figure can be found among literature data. For example, Saveant and Tessier^{1a} arrived at the mean value of $\partial\alpha/\partial E = 0.45$ for electroreduction of benzaldehyde in ethanol.

It seems that the reciprocal value, $\partial E/\partial\alpha$, may also be considered to have a physical meaning. It is the range of potential necessary to sweep up in order to observe the whole range of transfer coefficient variability, from 0 to 1. In this work, the value of $\partial E/\partial\alpha = 2.38$ V was obtained, whereas for the data taken from literature^{1a} the value was 2.22 V.

Acknowledgement

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