POLAROGRAPHIC REDUCTION OF ESTERS OF ARENESULFENIC ACIDS

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Investigating the behavior of esters of nitrobenzenesulfenic acids in reactions of electron transfer, we undertook to determine the sequence of the polarographic reduction of the sulfene ester and nitro group, simultaneously present in the molecule. For this purpose we studied the polarographic behavior of methyl and n-propyl benzenesulfenates, as well as 2-nitro-, 4-nitro-, and 2-nitro-4-chloro-substituted methylbenzenesulfenates in anhydrous DMFA.

On the polarograms of methyl and n-propyl esters of benzenesulfenic acid in DMFA, with tetraethylammonium iodide as the supporting electrolyte, three waves are observed with $E_{1/2}$ −1.3 V and the basic wave with $E_{1/2}$ −1.99 V (Fig. 1 and Table 1; all the potentials are cited relative to an aqueous saturated calomel electrode). The height of the basic wave is 3-3.5 times as great as the height of the prewave. A comparison of the summary heights of these waves with the height of the wave on the polarogram of iodobenzene, obtained under the same conditions, shows that the reduction of the sulfenate group corresponds to a two-electron process. From a graph of E versus log $i/(i_d-i)$ it follows that the process is irreversible. The slope of a straight line in the indicated coordinates is 115 mV. The limiting current of the prewave is not a diffusion current. This is evidenced by the absence of a linear relationship between the height of the prewave and the concentration of the depolarizer, as well as the absence of proportionality between the changes in this height and $h^{1/2}$ (h is the height of the mercury column). For the sum of the indicated waves, such dependences are linear. Consequently, the summary limiting current is of a diffusion nature.

These data agree with the results of [1], obtained for methyl phenylsulfenate in aqueous alcohol medium: there is an irreversible reduction with the participation of two electrons

$$C_6H_5SOCH_3 + 2e \rightarrow C_6H_5S^- + CH_3O^-$$

The appearance of a prewave may be associated with the formation of readily reduced particles on the mercury surface, for example, $C_6H_5SHgHgSC_6H_5$. The concentration of these particles is limited by the surface area of the electrode, which can explain the observed properties of the prewave.

The introduction of acceptor substituents into the benzenesulfenate molecule leads to a displacement of the waves into the region of less negative potentials (see Table 1). Just as in the case of esters of benzenesulfenic acid, 2-nitro-, 4-nitro-, and 2-nitro-4-chloroderivatives each give two waves on the polarogram, and the first wave is approximately half the height of the second (Fig. 2). However, for nitroderivatives the limiting currents not only of the second, but also of the first wave are of a diffusion type. For the methyl ester of 2-nitrophenylsulfenic acid, a linear dependence of the height of the first wave both on $h^{1/2}$ and on the concentration of the depolarizer (the quantity $d(i_d)/dC = 3.62$; for iodobenzene 3.26 μA /mmole) is observed. The first wave is close in height to the wave of the reduction of iodobenzene, taken in the same concentration. Evidently, the first step corresponds to two-electron reduction of methyl 2-nitrobenzenesulfenate. The slope of the first wave in a plot of E versus log $i/(i_d-i)$ is close to 60 mV. For the second wave the quantity $d(i_d)/dC = 11.2$ μA/mmole, i.e., on the second wave twice as many electrons are transferred. Thus, the total number of electrons consumed for the reduction of one molecule

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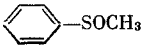
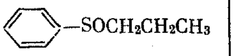
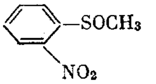
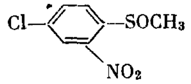
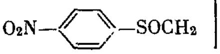
TABLE 1. Half-Wave Potentials ($-E_{1/2}$) of Arenesulfenates ($3 \cdot 10^{-4}$ M) in DMFA; Background 0.1 M $(C_2H_5)_4NI$, 25°

Compound	$-E_{1/2}$, V (relative to saturated calomel electrode)	
	first wave	second wave
	1,99 *	Absent
	2,03 *	*
	0,92	1,72
	0,91 †	1,51 †
	0,82	1,60
	1,20	1,85

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*After a prewave with $E_{1/2} \sim -1.3$ V.

†With a 0.1 M $NaClO_4$ supporting electrolyte.

of methyl 2-nitrophenylsulfenate is equal to 8. On the polarogram of methyl 4-nitrophenylsulfenate, two waves are also observed; moreover, the first corresponds to a transfer of two electrons per molecule, while the second corresponds to a transfer of approximately five (i.e., from four to six electrons).

The addition of phenol (8.5 mole %) to a solution of methyl 2- and methyl 4-nitrophenylsulfenates in DMFA does not change the ratio of the heights of the waves, but it shifts $E_{1/2}$ of the second wave by 300-400 mV into the region of less negative potentials (see Fig. 2). In this case the value of $E_{1/2}$ of the first wave is unchanged. In the presence of water (4 mole %), $E_{1/2}$ of the first wave of methyl 2-nitrophenylsulfenate is also unchanged, while the second wave is separated into two different components; the ratio of the heights of the waves is 1 : 1.5 : 1.5. The half-wave potentials of the first and third waves of reduction in the presence of water are equal to the potentials in abs. DMFA; $E_{1/2}$ of the second wave is almost 150 mV less negative than that of the third.

The data presented agree with the assumption that the first electrochemical step in the reduction of nitroarenesulfenates is the cleavage of the sulfene ester bond. Such a process should correspond to the transfer of two electrons; evidently it proceeds without the participation of a proton, and therefore, the half-wave potential should not depend on the accessibility of the proton. If the second step corresponds to the reduction of the nitro group, it should be a four- or six-electron process and depend on the presence of proton donors, since it includes the process of preliminary protonation [2]. As it follows from the results obtained, the second waves on the polarograms of nitrosulfenates are multielectronic, while $E_{1/2}$ of these waves become less negative after the addition of phenol. This is also indicated by a comparison of the polarograms of the methyl ester of 2-nitrobenzenesulfenic acid in DMFA, obtained with tetraethylammonium or sodium perchlorate as the supporting electrolyte (see Fig. 2). A change in the nature of the cation of the supporting electrolyte has no effect on $E_{1/2}$ of the first wave; however, it has a strong effect on the potentials of the second multielectronic step (compare the table data). The replacement of the tetraethylammonium cation by Na^+ leads to a less negative $E_{1/2}$ of the second wave (by almost 200 mV). Thus, the introduction of Na^+ into the system increases the stability of the particles formed at the second (but not at the first!) step of the reduction. The result obtained is entirely understandable on the assumption that the nitrogen group is reduced at the second, and not at the first step.

To verify the correctness of this assumption, we conducted a partial macroelectrolysis of the methyl ester of 2-nitrobenzenesulfenic acid on a mercury cathode at a potential somewhat more negative than $E_{1/2}$. Just as in polarography, DMFA was used as the solvent, while Na or tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte. After electrolysis and treatment of the solution obtained with CH_3I, a mixture of the initial nitrosulfenate and 2-nitrothioanisole was isolated. The products corresponding to the reduction of the nitro group were not detected.

Thus, in nitrosubstituted arenesulfenates, the sulfene ester group is reduced earlier than the nitro group. From this it might have been concluded that the sulfene ester group is more active in reactions of

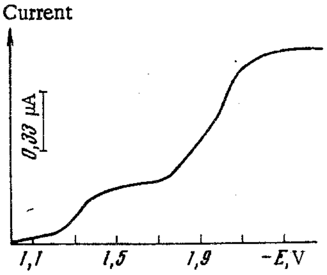

Fig. 1

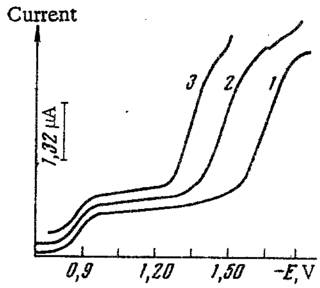

Fig. 2

Fig. 1. Polarogram of the methyl ester of benzenesulfenic acid ($2 \cdot 10^{-4}$ M) in DMFA with a 0.1 M $(C_2H_5)_4NI$ supporting electrolyte.

Fig. 2. Polarograms of the methyl ester of 2-nitrobenzenesulfenic acid ($3 \cdot 10^{-4}$ M) in DMFA with supporting electrolytes: 1) 0.1 M $(C_2H_5)_4NI$; 2) 0.1 M $NaClO_4$; 3) 0.1 M $(C_2H_5)_4NI$ in the presence of 8.5 mole % phenol.

electron transfer than the nitro group. However, under polarographic conditions, the specific interaction of the sulfur-containing group with the surface of the mercury electrode, which lowers the activation energy of the process, might have an influence on the sequence of the reduction. Let us note that the compounds studied are very difficult to reduce on a rotating platinum electrode in DMFA or in CH_3CN (at potentials ~—1.8 V). A study of the transfer of electrons to nitroarenesulfenates in homogeneous medium, using the dipotassium salt of the cyclooctatetraene dianion in THF as the donor, showed [3] that the sulfene ester group is less active than the nitro group.

It can be concluded that the sequence of reduction of electrochemically active groups, simultaneously present in the molecule, depends on the nature of the electron donor. This must be taken into consideration in a comparison of the acceptor capacity of various functional groups.

EXPERIMENTAL METHOD

Starting materials: methyl benzenesulfenate [4], bp 102° (6 mm). n-Propyl benzenesulfenate exhibits a triplet with $\delta_{\alpha\text{-}CH_2}$ 3.62, $\delta_{\beta\text{-}CH_2}$ 1.60, δ_{CH_3} 0.89 ppm and a multiplet with $(\delta_{C_6H_5})_{av}$ 7.23 ppm, with an intensity ratio 2 : 2 : 3.4 : 4.7, in the PMR spectrum. Methyl 2-nitrobenzenesulfenate [5], mp 52-53°. Methyl 4-nitrobenzenesulfenate [6], mp 46°, unstable and rapidly converted in solution to 4,4'-dinitrodiphenyldisulfide. The polarograms of methyl 4-nitrobenzenesulfenate were verified each time with the polarograms of 4,4'-dinitrodiphenyldisulfide. Methyl 2-nitro-4-chlorobenzenesulfenate was produced by us for the first time: 2 g (0.009 mole) of 2-nitro-4-chlorophenylsulfene chloride with mp 99° [7] was mixed at ~20° with 20 ml of methanol, and 0.5 g (0.009 mole) of CH_3ONa powder was gradually added; the mixture was mixed for another 2 h, and at 0° the precipitate was filtered off and crystallized from n-hexane. Shining yellow plates with mp 109-110° were obtained, yield 1.2 g (63%). Found: C 38.40; H 2.69; N 6.33; Cl 16.45; S 14.99%. $C_7H_6ClNO_3S$. Calculated: C 38.32; H 2.76; N 6.39; Cl 16.15; S 14.61%.

Polarographic measurements were conducted at 25 ± 0.5°. The dropping period of the capillary with an open circuit was 3.6 sec. Polarograms were recorded on an LP-60 polarograph; the potential of the working electrode was measured relative to an aqueous saturated calomel electrode with a PPTV-1 potentiometer. To determine the dependence of the height of the waves on the concentration of the depolarizer, we prepared solutions containing from $1 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ M methyl phenylsulfenate.

Preparative electrolysis of methyl 2-nitrophenylsulfenate was conducted in a 0.1 M solution of $(n\text{-}C_4H_9)_4NClO_4$ or $NaClO_4$ in anhydrous DMFA, in a cell with a cellophane membrane. The membrane was exposed to the solution of the supporting electrolyte for 2 h before the experiments. The potential of the working electrode (mercury, 25 cm^2) was set and maintained with a P-5848 potentiostat. Electrolysis was conducted at a potential of —1.00 V in 40 ml of the background solution. As a rule, 0.270 g of the substance was taken for one experiment. During electrolysis the solution was mixed continuously with a magnetic mixer in a stream of argon. The background current at —1.00 V was from 3 to 5 mA, the current at the beginning of electrolysis 80-100 mA. During electrolysis the color of the cathodic solution gradually changed from orange to cherry red, and then to greenish-blue. After electrolysis (drop of the current of electrolysis to the current of the supporting electrolyte) with a counter-current of Ar, 0.2-0.5 ml of pure CH_3I, purged with argon, was injected into the solution with a syringe. The solution thereupon acquired an orange color. Chromatography on a thin layer of Al_2O_3 revealed 2-nitrothioanisole and methyl 2-nitrophenylsulfenate (eluents hexane : THF, 4 : 1). After the solvent was distilled off, 0.11 g of a yellowish powder was obtained. The powder was dissolved in hexane and filtered hot. After cooling 0.02 g of methyl 2-nitrophenylsulfenate, mp 52-53°, was obtained. After removal of the sulfenate, the filtrate was evaporated and the residue recrystallized from water. Yield 0.04 g 2-nitrothioanisole (light yellow needles) with mp 60-61° (64-65° [8]). A mixed sample of the isolated substances with samples of known structure gave no depression of the melting point.

CONCLUSIONS

1. The electrochemical reduction of esters of arenesulfenic acids in dimethylformamide leads to cleavage of the sulfene ester groups.

2.. In nitroderivatives of arenesulfenates, reduction of the SOR group on a dropping mercury electrode occurs earlier than that of the nitro group.

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