

Substituent Effects of Sulfur Groups

II. The Polarographic Reduction of the $-S-O-$ Linkage, with Special Reference to Methyl Benzenesulfenate

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In recent times the polarographic reduction of the $-S-S-$ linkage with the sulfur partners in various oxidation states have been studied by various authors, and it has been found that a fission of the $S-S$ bond always is involved in the reduction mechanism. Studies on the $-S-S-$,¹ $-SO-S-$,^{1,2} $-SO_2-S-$,^{1,2} and $-SO_2-SO_2-$ ³ linkage have for example been reported. It has also been found that the $-S-O-$ linkage is reduced with fission of the $S-O$ bond, and it seems of great interest to compare the polarographic behaviour of the $-S-S-$ linkages with that of their oxygen analogues.

It has previously been reported that the $-SO_2-O-$ linkage is reduced with fission of the $-S-O-$ bond.⁴ In the study of the substituent effects of sulfur groups on the polarographic reduction of the nitro group in substituted nitrobenzenes described in the first paper of this series,⁵ it was found that in the polarographic reduction of nitrobenzenesulfonic acid esters both the nitro and ester groups were reduced. The reduction of the $-SO-O-$ linkage takes place in a four electron irreversible reduction step with fission of the $S-O$ bond, and the data are consistent with a reduction mechanism, analogous to that of the $-SO-S-$ linkage. Similarly, when studying the *o*-nitrobenzenesulfonic acid ester, it was found that in this case as well the $-S-O$ linkage is reduced, and in the present communication observations made in the polarographic study of substituted benzenesulfonic acid esters will be preliminarily reported, using the unsubstituted methyl benzenesulfenate as an example.

Measurements were made in three different solutions containing 25 % ethanol (acetate buffer, pH 5.0, phosphate buffer, pH 7.2, and ammonia buffer, pH 9.3). The reduction takes place irreversibly in a diffusion controlled 2 electron step. This suggests the over all mechanism I. Polarograms recorded at pH 5.0 are shown in Fig. 1 and the electrocapillary curve at pH 7.2 in Fig. 2. In the polarograms

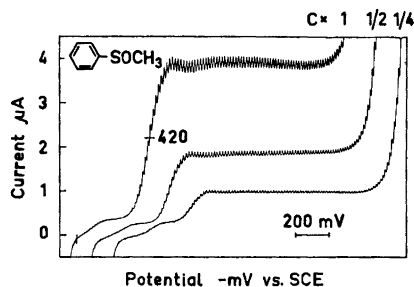


Fig. 1. Polarograms for methyl benzenesulfenate in acetate buffer, pH 5.0, conc. $C \times 1 = 10^{-3}$ M.

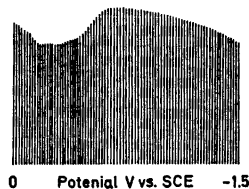


Fig. 2. Electrocapillary curve for methyl benzenesulfenate in phosphate buffer, pH 7.2, conc. 5×10^{-4} M.

splitting of the waves is observed, indicating a stepwise reduction with adsorption of intermediate products. The pre-wave in Fig. 1 seems to be a typical adsorption wave and the electrocapillary curve exhibits strong electrocapillary activity also suggesting adsorption phenomena.

The first step of the reduction could possibly be a reductive fission of the $S-O$ bond leading to the formation of the

same intermediate as is formed in the currentless prereaction observed in the reduction of disulfides⁶ (IIa). This intermediate is known to be strongly adsorbed in the form of a mercury compound giving rise to adsorption waves. In the reduction scheme proposed for the present case, it is a reduction intermediate instead of the depolarizer that is adsorbed, and hence an adsorption pre-wave, as seen in Fig. 1 would be expected. In the next step the mercury intermediate is reduced in the same manner as in the case of disulfides (IIb).

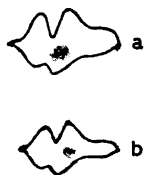
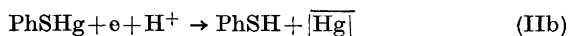
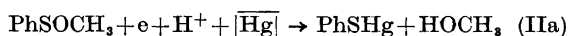
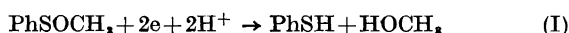


Fig. 3. Oscillographic $dE/dt-dE$ curves for a) methyl benzenesulfonate, b) benzenethiol in phosphate buffer, pH 7.2, conc. 10^{-5} M.

In Fig. 3a a $dE/dt-dE$ curve is shown, which is very similar to that of thiophenol, Fig. 3b. The anodic part shows an incision suggesting the anodic oxidation of thiol formed according to IIb, which further supports the proposed mechanism.

The proposed reduction mechanism is analogous to that of the polarographic reduction of seleninic acids,⁷ and from the mechanistic point of view, this reduction constitutes an interesting intermediate between the reduction of disulfides and peroxides.⁸ It is composed of two one electron reduction steps, each representing parts of the reduction mechanisms occurring in the other two systems.

As a new example in the series of $-S-S-$ linkages, the linkage $-S-SO_3^-$ was added. It shows a very irreversible wave with a very negative half-wave potential, Fig. 4, as compared with the other $-S-S-$ linkages (charge effect).

A summary of polarographic data of interest for the comparison of the reduction of the $-S-S-$ and $-S-O-$ linkages is given in Table 1. From the data shown it is obvious that the series of alkyl substituted $-S-S-$ linkages and the series of *S*-aryl *O*-alkyl substituted $-S-O-$ linkages can be classified as analogous with regard to the polarographic reduction mechanism.

Further, it may also be observed that for the *S*-aryl *O*-alkyl esters the half-wave potential is shifted about 1 V towards

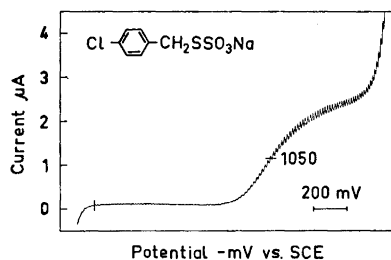


Fig. 4. Polarogram for sodium *p*-chlorobenzyl-*S*-thiosulfate in phosphate buffer, pH 7.2, conc. 5×10^{-5} M.









the negative side for each additional oxygen, and also that the slope of the waves increases with increasing oxygenation. Thus it seems that an increased degree of oxygenation decreases the accessibility of the linkage for electron transfer.

Polarography. The experimental conditions were similar to those in Ref. 5.

Methyl benzenesulfonate was prepared according to Lecher.⁹ (Found: S 22.7. Calc. for C_7H_7OS : 22.9.)

p-Tolyl α -disulfone was prepared according to Hilditch,¹⁰ m.p. $\sim 210^\circ$ (decomp.) Lit. $210-21^\circ$ decomp. It was for solubility reasons measured in methanol containing 10% benzene by volume, 0.1 M in $(\text{CH}_3)_4\text{NBr}$ and 0.05 M in acetic acid.

Table 1. Comparison of the polarographic reduction of various -S-S- and -S-O- linkages.

Linkage investigated	Number of electrons	E_1 , V pH 7.2	Bonds reduced	Reversibility	Ref.
	2		2 × S-Hg	rev.	1
Ar-S-S-Ar	2		2 × S-Hg	rev.	6
R-S-S-R	2		S-S	irrev.	1
R-O-S-Ar	2	-0.50	O-S S-Hg	irrev.	
	4		S-S SO	irrev.	1,3
	4	-1.4	O-S SO	irrev.	5
	2		S-S	irrev.	1,3
	2	< -2.2	O-S	irrev.	4
	2		S-S		3
	2	-0.65	S-S	irrev.	
	2	-1.05	S-S	very irrev.	

Ar¹=*p*-tolyl; Bz¹=*p*-chlorobenzyl

Sodium *S-p*-chlorobenzyl thiosulfate was prepared by treating *p*-chlorobenzyl chloride with sodium thiosulfate in aqueous ethanol.¹¹ (Found: S 24.5. Calc. for C₇H₆ClO₂SNa: S 24.6).

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