

Anodic Oxidation of Benzenesulfinate Ion

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In methanol, benzenesulfinate ion gives an anodic polarographic wave.¹ The cathodic reduction of aromatic sulfinic acids has been studied in aprotic medium.² The sulfinate ions are not reduced under such conditions. In order to ascertain whether the anodic reactions of benzenesulfinate ion are useful in (1) the quantitative determination of benzenesulfinate ion and/or (2) the preparation of diphenyl disulfone we have investigated the anodic behavior of benzenesulfinate ion and benzenesulfinic acid in more detail. Voltammetry and coulometry at controlled potential were applied at the mercury electrode and the glassy carbon electrode (GCE) in acetonitrile (AN), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

In all the three solvents an anodic peak appeared at 0.5 V in the voltammograms of benzenesulfinate ion at a stationary GCE (Fig. 1a). The peak current was proportional to the concentration and to the square root of the potential scan rate and corresponded to an oxidation by 1 F/mol. (The diffusion coefficient was estimated from the polarographic limiting current and the transfer coefficient (α) from the dependence of peak potential on potential scan rate.) In the cathodic scan of the cyclic voltammograms at GCE a small peak appeared at -1.1 V due to the reduction of diphenyl disulfone (Fig. 1a). The benzenesulfinate ion dissolved in AN decomposed slowly, and DMF and DMSO should be preferred for quantitative determinations. The anodic peak potential of 1 mM benzenesulfinic acid in AN was 1.5 V. In the coulometric experiments with benzenesulfinate ion only 10–20 % of

the initial amount of sulfinate ion was converted to diphenyl disulfone ($\text{PhSO}_2\text{SO}_2\text{Ph}$, Table 1). The other products of the electrolysis were not identified. An attempt to detect benzenesulfonate ion was not successful. In AN at the oxidation potential $E=0.5$ V an apparent value of $n=0.6$ F/mol had been consumed in the electrode reaction, when the current dropped to the background value of the supporting electrolyte. When the oxidation potential was increased to $E=1.7$ V (more positive than the oxidation potential of benzenesulfinic acid) 1.9 F/mol were exchanged with no formation of diphenyl disulfone (Table 1). Only 2 mmol (20 %) of diphenyl disulfone were isolated in a coulometric experiment, where 20 mmol of benzenesulfinic acid were oxidized in DMF at $E=0.9$ V with $n=1.5$ F/mol. 1 F/mol was consumed in the coulometric experiments with benzenesulfinate ion at the Hg pool (Table 1). Polarographic curves together with UV spectra of the electrolysis product and mercury(II) benzenesulfinate ($\text{Hg}(\text{SO}_2\text{Ph})_2$) were identical, confirming that a mercury(II) compound is formed in the anodic process of benzenesulfinate ion at the mercury electrode. The presence of mercury in the product of the electrolysis was proved by atomic absorption spectroscopy too (Table 1). In all the three solvents the polarographic half-wave potential of benzenesulfinate ion was 0.1 V. The limiting current was proportional to the concentration and polarography as well as voltammetry at GCE should be convenient methods for the quantitative determination of benzenesulfinate ion in aprotic solvents. The voltammetric peak currents at the hanging mercury drop electrode and the polarographic limiting currents corresponded to a consumption of 1 F/mol in the anodic process of benzenesulfinate ion at the mercury electrode. For benzenesulfinate ion as well as mercury(II) benzenesulfinate the potential difference between the anodic and the cathodic peaks in the cyclic voltammograms at a hanging mercury drop (Fig. 1b) and the slope of the

Table 1. Coulometric experiments with sodium benzenesulfinate at the glassy carbon electrode (GCE) and the mercury electrode at constant potential (E) and determination of diphenyl disulfone and mercury(II) benzenesulfinate in the product of the electrolysis. n = the apparent number of electrons consumed in the electrode reaction.

PhSO_2^- / μmol	Solvent	Electrode material	E / V vs. SCE	n / F mol ⁻¹	$\text{PhSO}_2\text{SO}_2\text{Ph}$ / μmol	$\text{Hg}(\text{SO}_2\text{Ph})_2$ / μmol
20	AN	GCE	0.5	0.62	1.2	—
20	AN	GCE	1.7	1.9	0	—
30	DMF	GCE	0.8	1.1	3.1	—
10	AN	Hg	0.3	0.95	—	^a
32	DMF	Hg	0.3	0.97	—	15
16	DMF	Hg	0.3	0.99	—	8

^a Not analyzed.

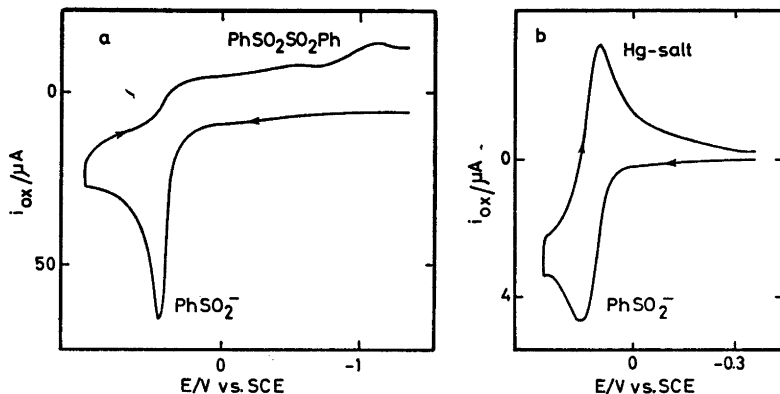


Fig. 1. Cyclic voltammograms of sodium benzenesulfinate. (a) 2.6 mM in DMF, 0.1 M TEAP, at a glassy carbon electrode and scan rate 0.2 V s^{-1} . (b) 1.0 mM in DMSO, 0.1 M TEAP, at a hanging mercury drop electrode and scan rate 0.05 V s^{-1} .

polarographic waves were consistent with a fast 1-electron process. The polarograms of mixtures of sodium benzenesulfinate and mercury(II) benzenesulfinate showed one composite anodic-cathodic wave indicating that benzenesulfinate ion-mercury(II) benzenesulfinate constitute a reversible redox system at the mercury electrode. Since the cyclic voltammograms at the hanging mercury drop electrode and the polarograms of benzenesulfinate ion as well as mercury(II) benzenesulfinate were characteristic of a reversible 1-electron process it may be assumed that the electron transfer proceeds over a mercury(I) compound. The intermediate formation of a mercury(I) compound followed by disproportionation to a mercury(II) compound has been suggested also for the anodic polarographic processes of dialkyldithiocarbamates in aqueous solutions.³ In aprotic solvents another type of polarographic behavior is shown by the thiophenolate ion-mercury(II) thiophenolate system, which gives rise to two polarographic waves due to the formation of $\text{Hg}(\text{SPh})_2^-$ as a stable intermediate.⁴

Experimental. Sodium benzenesulfinate (Fluka, *purum*) was used after drying in vacuum at 60°C . Benzenesulfonic acid was precipitated from a sulfinate water solution by conc. sulfuric acid, washed and dried at room temperature. Diphenyl disulfone (m.p. $192-194^\circ\text{C}$) was prepared according to the method of Hilditch.⁵ Mercury(II) benzenesulfinate precipitated from an aqueous solution of mercury(II) acetate and sodium benzenesulfinate. The precipitate was washed with water and ethanol and contained 41.8 % Hg. The water content of the organic solvents under experimental conditions was 0.1–0.2 % as determined by gas chromatography.

A PAR Model 170, Electrochemistry System, was used for the electrochemical measurements. All potentials given refer to the SCE. The glassy carbon electrode (Chemtrix Inc.) had a geo-

metrical area of 7 mm^2 . The concentration range investigated in the voltammetric measurements was 0.10–3.0 mM and the solutions contained 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The temperature was $25.0 \pm 0.1^\circ\text{C}$. The coulometric experiments were carried out in a volume of 5–10 ml in a glassy carbon beaker or over a Hg pool. Diphenyl disulfone was analyzed in the product of the electrolysis by polarography ($E_{1/2} = -0.8 \text{ V}$) and mercury(II) benzenesulfinate by atomic absorption spectroscopy (Varian Techtron, Model 1000). The large scale electrolysis of benzenesulfonic acid (2.9 g) at GCE was performed in an undivided cell with a rotating platinum disk as a counter electrode. A white solid precipitated when the electrolyzed solution was diluted with water. The precipitate was dissolved in diethyl ether and washed with acid and neutral aqueous buffer solutions. The organic phase was evaporated and 0.56 g of electrolysis product was obtained. Melting points and also UV spectra (Pye Unicam SP 1800) of the isolated product and diphenyl disulfone were identical. In the coulometric experiments with sodium benzenesulfinate at the mercury electrode UV spectra (in AN) and polarograms were recorded without isolating the mercury(II) benzenesulfinate formed in the electrode reaction.

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