

# On the Splitting of the Sulphonic Group from the Aromatic Ring by Electrolytic Reduction

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(Received February 24, 1932)

Some of the sulphonic groups attached to the aromatic ring can easily be removed by electrolytic reduction. For instance, *o*-sulphobenzoic amide was recently found in our laboratory<sup>1</sup> to undergo reduction electrolytically in an alkaline solution and produce benzamide with a yield of 65%. The facility with which the sulphonic group is thus split from the aromatic ring seems to be governed by the nature of the aromatic ring itself, and also by the properties and position of other radicals attaching to the ring. According to Friedländer and Lucht<sup>2</sup>  $\alpha$ -naphthalene sulphonic acid is reduced with sodium amalgam more easily than the corresponding  $\beta$ -compound. Some such points or even more minute ones may perhaps be investigated electro-chemically. As to electrolytic reduction, however, the works dealing with this subject are very scanty; the only instance we can find in chemical literature is that of the German patents<sup>3</sup> concerned in the process used for the elimination of some sulphonic radical from a polysulphonic compound.

In the research here reported, it was found that, the presence of an acidic radical such as COOH favours the splitting of the sulphonic radical in a benzene ring, while a basic radical like NH<sub>2</sub> acts contrarily. And even the influence of one and the same radical is not always the same, but is greatly altered by difference in the relative position of it and the sulphonic radical. In reduction of sulphobenzoic acids,

1. These Memoirs, series A, **15**, 155 (1932)
2. Ber., **26**, 3028 (1893).
3. D. R. P., 248527, 255724.

the o- and p-compounds are reduced with far greater ease than the corresponding m-compound, but in the case of sulphanilic acids, the m-compound is far more readily reduced than the p-compound.

All the reduction experiments described below were carried out with the lead cathode; the use of mercury instead of lead did not show much difference.

### Exmerimental

In all the experiments here described, caustic soda solutions were always used as the catholyte, to which sometimes alcohol was added to increase the solubility of the sulphocompound used for reduction. As the anolyte, a concentrated sodium carbonate solution was taken, and electrolysed with electrodes of lead.

#### 1. Benzenesulphonic acid

Three grams of the sodium salt were dissolved in 100 c.c. of 20% caustic soda solution, and the solution was electrolysed by passing a current of 2.4 amperes/60 sq. cms. at 25°. Shortly after the electrolysis commenced, benzene began to be evolved at the cathode, and at the same time the presence of sulphurous acid in the catholyte became recognizable. During the electrolysis, 5 c.c. of the cathode solution was taken out at intervals of an hour, and the amount of sulphurous acid was determined iodometrically in order to find how far the sulphonic acid had been reduced.

Time of electrolysis (Hours)	SO <sub>2</sub> (mg.)	Amount reduced (%)
2	18.8	35
3	20.4	38
4	20.9	39
5	20.9	39

The reduction was thus observed to have practically ended after 3 hours' electrolysis.

Influence of temperature.—Under exactly the same conditions as described above, another series of four experiments was made, a current of 4 amperes/sq. dm. being passed for 3 hours at different temperatures.

Temperature	Amount reduced (%)
15°	60
25°	39
55°	10
65°	4

The results show that high temperature has a deleterious effect on the reduction.

Influence of the current density.—Electrolysis was next conducted with currents of different density passed for 3 hours. The results were as follows :

Current density (amp./sq. dm.)	Conc. of NaOH (%)	Temp.	Amount reduced (%)
1.6—2.0	10	20°	trace
2.2	"	"	2.5
4.0	"	"	6.5
2.0	20	15°	6.8
2.5	"	"	25.0
4.0	"	"	60.0

High current density is thus seen to favour the reduction.

Influence of the concentration of alkali.—Caustic soda solutions of different degrees of dilution, in which 3 grams of benzene sulphonic acid were dissolved, were electrolysed.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Amount reduced (%)
5	6.0	2.4
10	4.0	6.3
20	4.0	39.0

From the above results so far described it became clear that high concentration of alkali, greater density of the current and low temperature are essential for electrolytic reduction of benzene sulphonic acid.

## 2. Sulphanilic acid

Electrolysis of sulphanilic acid was carried out under nearly the same conditions as in the case of benzene sulphonic acid, but no appreciable reduction could be observed.

### 3. Metasulphanilic acid

Two grams of the crystalline acid were dissolved in 100 c.c. of 5-20% caustic soda solution, and other conditions being kept nearly the same as in the case of benzene sulphonic acid, electrolysis was carried out. The results were as follows :

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2.0	21°	7	0
10	3.0	50°-70°	"	0
"	4.0	25°	4	26.0
20	"	"	2	37.0

For reduction of metasulphanilic acid high concentration of alkali and also high current density are essential conditions of electrolysis.

### 4. Paraphenolsulphonic acid

This acid could not be reduced electrolytically.

### 5. Orthosulphobenzoic acid

Three grams of the crystalline acid were dissolved in 100 c.c. of caustic soda solution of different concentrations, and the amounts of benzoic acid formed by the electrolysis were estimated. As is seen in the following table, low temperature was found to be the most important condition for this electrolysis.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
2	2.0	19°	4	59
5	"	"	6	77
"	"	55°-63°	5.5	56
10	3.0	22°	5	63

### 6. Metasulphobenzoic acid

Two grams of sodium metasulphobenzoate were electrolytically reduced in caustic soda solution, and the amounts of benzoic acid formed were determined with the following results :

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2.0	10°	2	37
"	"	25°	"	"
"	"	62°	"	21
"	4.0	25°	1.5	38
10	"	"	2	36

Reduction of *m*-sulphobenzoic acid also depends chiefly on temperature, and is not much affected by either concentration of alkali or current density, if the temperature is kept below 25°.

### 7. Parasulphobenzoic acid

The sodium salt of this acid was electrolysed in the caustic soda solution with the following results:

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Amount reduced (%)
5	2	25°	2	77
"	4	62°	"	74
10	4	25°	"	77

High temperature tends to lower the reduction efficiency somewhat.

### 8. $\alpha$ -Naphthalenesulphonic acid

Electrolysis was sometimes conducted with the alcoholic caustic soda solution, as the sodium sulphonate is soluble only with difficulty in a concentrated caustic soda solution. After about 15 minutes'

Catholyte			Current density (Amp./sq. dm.)	Temp.	Amount reduced (%)
NaOH (g.)	H <sub>2</sub> O (c.c.)	C <sub>2</sub> H <sub>5</sub> OH (c.c.)			
—	100	—	1.7	20°	3.8
5	90	10	2.0	15°	8
"	"	"	2.5	45°	23
"	100	—	4.0	25°	17
5	100	—	4.0	50°	39
10	70	30	2.5	35°	23
"	80	20	4.0	25°	38
"	"	"	"	55°	52
"	"	"	5.0	25°	36

electrolysis naphthalene began to separate out. To prevent loss of naphthalene by volatilization, a round-bottomed flask containing cold water was placed on the cylindrical cell which was used as the cathode compartment. The amount of the acid reduced was calculated from that of sulphurous acid determined iodometrically.

Unlike the case of reduction of benzene sulphonic acid and sulphobenzoic acid, high temperature favours the reduction of  $\alpha$ -naphthalenesulphonic acid.

### 9. $\beta$ -Naphthalenesulphonic acid

The sodium salt of the sulphonic acid was electrolysed in exactly the same manner as in the case of the corresponding  $\alpha$ -compound; the results were as follows:

Catholyte			Current density (amp./sq. dm.)	Temp.	Amount reduced (%)
NaOH (g.)	H <sub>2</sub> O (c.c.)	C <sub>2</sub> H <sub>5</sub> OH (c.c.)			
—	100	—	1.4—2.0	15°	3.8
5	75	25	1.4	"	6.2
"	100	—	4.0	25°	11.1
"	"	—	"	50°	5.7
"	65	35	2.8	20°	3.0
10	50	50	1.4	15°	3.8
"	"	"	2.5	50°	3.8
"	70	"	4.0	25°	14.0

When compared with the  $\alpha$ -compound reduction of  $\beta$ -naphthalenesulphonic acid is far more difficult than that of the  $\alpha$ -compound, and is somewhat retarded or at least not promoted by high temperature.

### 10. Naphtholsulphonic acids

Of the naphtholsulphonic acids such as 1:2, 1:4, 1:5 and 2:6, only 1:4 and 1:5 could be reduced, with a yield of about 10% of  $\alpha$ -naphthol, by passing a current of 4 amperes/sq. dm. into 10% caustic soda solution; the 1:2 and 2:6 acids remained quite unaffected. In electrolysis of disulphonic acids though slight formation of sulphurous acid could be perceived, yet not even a trace of the reduction product was procured.

## 11. Naphthionic acid

Sodium naphthionate was electrolysed in the caustic soda solution for 4 hours. After the electrolysis was over, the  $\alpha$ -naphthylamine separated out from the catholyte and also that remaining in the dissolved state were collected and weighed. As a result, naphthionic acid was found to undergo reduction comparatively well, especially when a current of high density was applied, thus—

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Yield of $\alpha$ -naphthylamine (%)
3	1.4	20°	trace
10	2.0	25°	21
"	4.0	"	72
"	"	60°	81

## 12. Naphthylaminesulphonic acid 1:5

Reduction of this acid in the caustic soda solution was found to proceed rather smoothly at high temperature, thus—

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Time of electrolysis (Hours)	Acid reduced (%)
10	2.5	18°	4	6
"	"	65°	"	73

## 13. Cleve's salt

A mixture of naphthylaminesulphonic acids 1:6 and 1:7, known as Cleve's salt, could not be reduced.

## 14. Naphthylaminesulphonic acid 2:5

After electrolysing the caustic soda solution of the acid for 2.5 hours the catholyte was nearly neutralised with hydrochloric acid, and the slightly alkaline solution thus formed was distilled with superheated steam, when  $\beta$ -naphthylamine melting at 106° was obtained as scaly crystals.

Conc. of NaOH (%)	Current density (Amp./sq. dm.)	Temp.	Amount reduced (%)
5	4.0	40°-45°	12
10	"	16°	"

### 15. Naphthylaminesulphonic acid 2:6

After electrolysis the presence of sulphurous acid in the catholyte could be detected, but the amount of  $\beta$ -naphthylamine produced by reduction was so small that its determination was impracticable.

### 16. Amidonaphtholsulphonic acids

Monosulphonic acid 2:6:8 and disulphonic acid 1:8:3:6 were subjected to electrolysis, but no recognizable reduction took place.

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